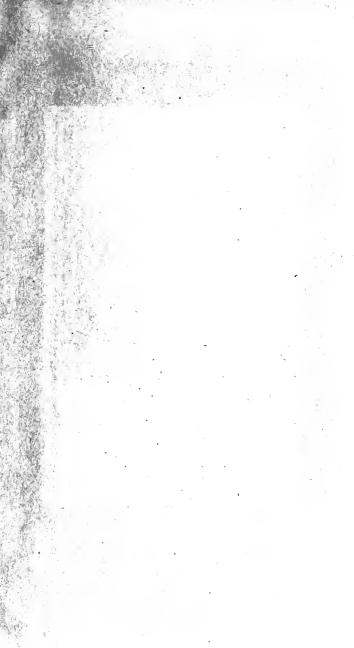
AN ENGRYPHICAL COMESE.







AN EXPERIMENTAL COURSE

OF

CHEMISTRY

FOR AGRICULTURAL STUDENTS

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Arnold's Practical Science Manuals

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AN EXPERIMENTAL COURSE

OF

CHEMISTRY

FOR AGRICULTURAL STUDENTS

ΒY

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EDITOR'S PREFACE

In the present state of scientific education, or, more correctly speaking, education in science, in this country, the instructor is frequently called upon to face the problem of teaching a particular science to students engaged or about to be engaged in some special industry. The problem is confessedly a difficult one to deal with practically, and many diverse views are held respecting its feasibility, or even the desirability of attempting its solution. The diversity of opinion no doubt represents the differences in the mode of treatment to which the various branches of science lend themselves. To the majority of educationists it is evident that instruction in science is, as a mental discipline, of a very high order of importance, quite apart from any technical knowledge relation to any special industry. More particularly does this apply in the case of those occupied in productive industries of all kinds, whether manufacturing or agricultural, in the widest meaning of the term.

Starting with the very reasonable assumption that those who are concerned with agriculture should know, at least, something of the general principles of chemical science, the question presents itself to all who are interested in the welfare of agriculture—How and When is such instruction to be given? The elementary schools, especially in country districts, are confessedly feeble in their science teaching, even if they attempt it at all. There is a crying need for good secondary and technical schools in rural centres, but little progress has as yet been made in this direction. That sound instruction in scientific principles by scientific method should be made

a part of the early training of boys and girls, is an ideal which we all hope to see realised; but so far as concerns the agricultural community, this ideal, although at present remote, must be seriously kept in view in any scheme of education having for its object the intellectual advancement of the British farmer.

In the meantime the County Councils, provided with the funds for Technical Education, have in many agricultural counties developed a laudable desire to improve the status of the agriculturalist by placing the means of acquiring sound instruction within his reach. In most parts of the country where such facilities have been offered, the younger generation of farmers have been found willing to avail themselves of them. Those counties which have failed hitherto to touch the agricultural community would do well to reconsider the policy which their Technical Instruction Committees have adopted.

With regard to a science of such fundamental importance as Chemistry, it is most desirable to arrest the attention and to arouse the interest of the student by enabling him to acquire his knowledge of general principles through practical work carried out in the laboratory with materials and by means of illustrations drawn as far as possible from sources with which his ordinary observation makes him daily familiar. This method may possibly lend itself to the criticism that it is wrong in principle to attempt too early a specialisation before the rudiments have been acquired. Nevertheless I am convinced that such a system can be successfully followed if judiciously carried out and not driven to the unwarrantable extreme of endeavouring to convert the agricultural student into an expert chemist.

The author of the present book has on these lines prepared a course of practical chemistry which has to my knowledge been most successful with agricultural students in the Central Laboratories of the Essex County Council at Chelmsford. At my suggestion he now offers this course to a wider public, and I can confidently recommend the work to all those who are practically engaged in teaching this science to a class of pupils whose welfare is so intimately associated with the progress of

chemical knowledge.

R. MELDOLA.

AUTHOR'S PREFACE

A FARMER does not need to be a chemist; at the same time he needs the training in accuracy, careful observation, and experimental method which a study of chemistry, properly carried out, imparts, and he needs a knowledge of the elementary principles of chemical change and of the properties of certain chemical substances, both inorganic and organic. The customary four years' course of inorganic and organic chemistry goes far beyond the requirements of an agricultural student, and is usually beyond the time at his disposal.

The following course is designed to enable an agricultural student to acquire the knowledge and training he needs by a short experimental study of the chemical substances with which agriculture is concerned, his attention being directed at the same time to the practical application of each subject dealt with to rural industry. The course upon which the work is founded has been in use during the past three years in some of the grammar schools and evening continuation schools in the rural districts of Essex, and has also been used in the County Technical Laboratories at Chelmsford by the students of the agricultural classes, and as a preparatory course for elementary school teachers who wish to qualify themselves to teach chemistry in the agricultural parts of the county.

In rural districts the introduction of the study of experimental science is often prevented by the costliness of apparatus and laboratory accommodation. With a view, therefore, to economy, the experiments have been designed for simple and inexpensive apparatus and chemicals. The

set required for twelve students, given in the Appendix, can be purchased for about £,40. Neither need the fitting of a laboratory for experimental work be a costly undertaking. A demonstration table, provided with drawers and a sink, working benches for twelve students, provided with a rack for reagents, fume cupboard, apparatus cupboard, shelves for chemicals, blackboard, balance shelf, and distillation table, also provided with a sink, together with gas and water supplies. constitute the equipment necessary, and cost from £50 upwards, according to the style of work. It is very desirable that for experimental work of this character the working benches should be so placed that the students face the demonstration table.

The course is divided into thirty-six experimental studies, through each of which the student, under the supervision of the teacher, is expected to work. Each student should work independently, and only in exceptional cases should two students be allowed to work together for a particular experiment. Each day's work should be accompanied by a revision Revision is quite as essential as the experimental work: for it is by this means that the teaching of each experiment is brought home to the student. It is desirable, and in the absence of revision necessary, that the student should answer in writing the questions and problems set. A written and practical examination should follow the conclusion of each part of the course. The sections on special subjects the teachers are recommended to expand into lectures to the class; it is not intended that the students should themselves make the experiments described in these sections.

The value of this course as a means of training will, to a large extent, depend upon the care, thoroughness, and accuracy with which the experimental work is carried out. In such work it is especially necessary to remember that

whatever is worth doing at all is worth doing well,

My thanks are due to Mr. F. HUGHES, who has kindly made the drawings for the figures which illustrate this volume.

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AN EXPERIMENTAL COURSE OF CHEMISTRY

FOR AGRICULTURAL STUDENTS

PART I

1. WEIGHTS AND MEASURES

In this course a knowledge of chemistry is to be sought by an experimental study of the composition and properties of those substances with which agriculture is concerned. In doing this it will be necessary to determine the *quantity* of substances both by weight and volume. In science a decimal system of weights and measures is employed. The standard of weight is the *gram*; the parts of the gram are the decigram, centigram, and milligram; the multiples are the dekagram, hectogram, and kilogram. By means of a chemical balance determine how many decigram and centigram weights make a gram and how many grams there are in a dekagram and hectogram.

In using a chemical balance observe the following rules:—Place the thing to be weighed in the left hand pan, the weights in the right. Never touch the weights with the fingers, but with the nippers only. Never place anything upon or remove anything from the pan while it is swinging. When reckoning up the weights do so while they are on the pan, then enter the amount in the notebook and check it by again counting the weights while returning them to the box.

As the names imply, it will be found that—

1 decigram = .1 gram. 1 dekagram = 10 grams.

ı centigram = .01 gram. ı hectogram = 100 grams.

1 milligram = .001 gram. 1 kilogram = 1000 grams.

The relations between this—the metric—and the avoirdupois systems are the following:—I gram = 15.432 grains; I ounce = 28.35 grams; I kilogram = 2.2 lbs.

The metric standard of length is the *meter*, the parts and multiples of which are similar to those of a gram. Examine a meter measure and note that—

1 decimeter = .1 meter. 1 dekameter = 10 meters.

1 centimeter = .01 meter. 1 hectometer = 100 meters.

1 millimeter = .001 meter. 1 kilometer = 1000 meters.

Of the relations between the metric and the British systems, I meter = 39.37 inches, I inch = 2.54 centimeters, I mile = 1.6 kilometers.

The standard of capacity is the *liter*. Examine a cube having a volume of 1 liter, and note that it is the measure of 1 cubic decimeter or 1000 cubic centimeters. Hence—

.001 liter = 1 cubic centimeter.

1 liter = 1 cubic decimeter.

1000 liters = 1 cubic meter.

Quantities measuring less than a liter are usually spoken of as so many cubic centimeters ("c.c."). Of the relations between the metric and British systems, I liter = 1.76 pints and I pint = 567 c.c.

A cubic centimeter of pure water measured at 4° C. weighs I gram. This simple relation between volume and weight provides a means of correcting the graduation of glass measures, these being often unreliable. Calibrate a 20 c.c. measure as follows:—Having cleaned and dried the measure, first weigh it empty. Then fill it with pure water from a wash bottle to the 10 c.c. mark and weigh again. Now fill it to the 20 c.c. mark and weigh a third time. Subtract the weight of the measure from the weight of the measure and water, in order

to find the weight of each 10 c.c. of water. Repeat the determination until uniform results have been obtained. measure correctly graduated, and are the two halves uniform?

Glass measures are usually graduated in such a way that each (so-called) cubic centimeter is the volume of I gram of water at 15° C. (the usual temperature of the laboratory), so that the water taken for the foregoing experiment should be at this temperature.

II. THE ATMOSPHERE

HAVING acquired a knowledge of the methods of determining

the quantity of substances, the study of the air may now be commenced. Firstly, has air

the property of weight?

Fit a liter flask with a cork, glass and indiarubber tubes, and glass stoppers as figured, and weigh it accurately upon the balance. Now remove one stopper, suck out the air as completely as possible, replace the stopper without readmitting air, and weigh again. the flask lost weight, and if so, what is the weight of air removed? Retain the apparatus for future experiments.



This experiment, in common with all scientific experiments, will only succeed if the apparatus is perfect. Practise cork-boring on old corks until true and clean bores can be made, and tube-bending on odd bits of glass tubing until the bends are rounded and regular. Start boring a cork from both ends so that the bores meet in the middle. To cut a glass tube draw a file once only across it and snap the tube with the fingers. To bend a tube use a fish-tail burner; hold the tube near the top of the flame, constantly turning it round, till the glass is soft; then remove and bend. Before pushing a glass tube through a cork, or fitting it with rubber tubing, always round off the sharp edges by just melting the glass in the Bunsen flame. Seal up the ends of a tube by melting in the Bunsen flame till the glass runs together; on now blowing through the open end the sealed end will expand into a little bulb.

By employing a stout glass flask which can be completely exhausted of air by means of an air-pump, the weight of a volume of air can be determined. Under normal conditions (see p. 39) a liter of dry air is found to weigh 1.226 grams. The atmosphere is known to extend in appreciable quantities to the height of one hundred miles above the earth, and its total weight and consequent pressure upon the earth's surface must be very great. What this amounts to can be ascertained by the following experiment:—

Fill a stout glass tube, at least 4 millimeters in bore, 8 decimeters long and closed at one end, with pure dry mercury.

Remove all bubbles of air by tapping the tube or other means, then close the open end with the finger and invert the tube into a capsule or trough containing mercury. Now remove the finger, and note that the mercury remains supported in the tube to a certain height. By means of a three-foot rule or meter measure, accurately determine the height of the column from the surface of the mercury in the trough. Compare the height with that in a tube of different length used by another student, and note that it is independent of the length of the tube Convey the apparatus to the top of the building, and note that, if 40 feet above the laboratory, the column

of mercury now supported is at least one millimeter shorter. This must be due to the smaller atmospheric pressure at the greater altitude; and the experiment shows that the mercury in the tube is balanced and supported by the atmosphere, and that its height is an accurate measure of the atmospheric pressure.

Whenever mercury is used, the experiment must be made on a tray or special table designed to catch falling particles. Without this precaution

great waste of mercury must occur even in experienced hands. The mercury used in the foregoing experiment must be perfectly dry.

This instrument is known as the *barometer* (weight-measurer). Owing to the relation that exists between the atmospheric pressure and the weather, it becomes a useful weather glass. Repeat the observation of the height of the mercury column

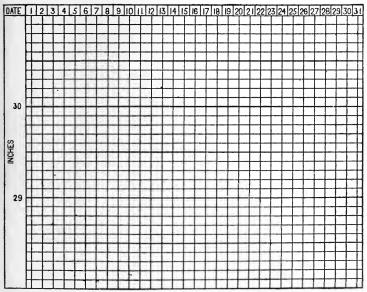


FIG. 3.

at the same hour daily for one month, marking each observation by means of a dot on the accompanying chart, and at the same time record the character of the weather (e.g. wind, rainfall, temperature, and sunshine) in the notebook. At the end of the period, connect the dots on the chart by straight lines, and compare the rise and fall with the variations in the weather.

At the level of the sea, the average height of the barometer is 30 inches or 760 millimeters, and this is taken as the normal or standard pressure. The old-fashioned weather glass consists of a . shaped barometer tube, in which a fall of the mercury in the long limb is accompanied by a rise of mercury in the short and open limb. Upon the surface of the mercury in the short limb is a metallic float connected by a cord with a wheel to which a pointer working against a dial is connected. The aneroid barometer consists of a partially exhausted box having a flexible side, and which expands or contracts with changes of pressure, the variation being exhibited by means of a dial and pointer. Such an instrument, being portable, is especially useful in determining altitudes by means of difference of atmospheric pressure. The action of the suction pump also depends upon the atmospheric pressure. Mercury being 131 times as heavy as water, it is theoretically possible to draw water from a depth 131 times as great as the barometric column. Owing, however, to dissolved gases and imperfect valves, 28 feet is the greatest depth from which it is practically possible to draw water by this means.

III. COMPOSITION OF AIR

To learn what air is, a careful study must be made of some of those changes which are observed constantly taking place in air, e.g. rusting and burning.

When iron rusts, the change which occurs might be due to absorption of air or of a constituent of it. If so, the weight of the rust would be greater than that of the

original iron, since air has weight. Place some iron filings in a capsule and weigh. Now expose the capsule to the air, and, when the filings have begun to rust, weigh again. Do the filings weigh more after rusting?

A further experiment is needed to determine whether air has actually disappeared. Shake some fine iron filings in a wide graduated tube, previously wetted with water so that the filings adhere to the side, and quickly invert the tube into a vessel of water.

Should the air in the tube diminish in volume in the course of a few hours, it must be concluded that the rust is the result of the absorption of air by iron.

Continue the experiment long enough to determine whether the air is entirely absorbed, and, if not, what are the proportions of the active and inactive constituents. Should only a portion of the air be absorbed, ascertain whether the unabsorbed part differs from the original air in any respect other than its inability to cause iron to rust. For instance, try whether it still supports the combustion of a taper. To do this, cover the orifice of the tube with a glass plate while under water, then remove the tube, turn up, and, having removed the plate, insert a lighted taper.

It is very important that (1) the object of each experiment, (2) the drawing and description of the apparatus, (3) every detail of the observations made, and (4) the conclusions arrived at, should be recorded in the student's notebook while the investigation is in progress. Weighings should be entered thus:—

```
Capsule and iron filings taken . . = 10.543 grams.
Capsule and iron filings after rusting . = 10.568 grams.
```

Increase of weight = .025 grams.

The measurements of volume of air should be recorded thus:—

Air in tube at 10 o'clock = 200 c.c. (experiment begun).

```
,, ,, II ,, = 190 c.c.

,, ,, 12 ,, = 180 c.c.

,, ,, 1 ,, = 170 c.c.

,, ,, 2 ,, = 160 c.c.

,, ,, 3 ,, = 158 c.c.

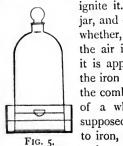
,, ,, 4 ,, = 158 c.c.
```

and the volumes of active and inactive constituents per cent. of air should then be calculated.

Should the preceding experiment indicate that the air, deprived of that portion which combines with the iron to form rust, no longer supports the combustion of a taper, it must be surmised that rusting and burning are phenomena of

a similar kind, and an experiment on combustion should now be made.

Cut under water a piece of phosphorus the size of a large pea, and after drying it by means of blotting paper (taking care not to touch it with the fingers on account of its inflammability), place it on a capsule floating in a trough of water, and ignite it. Place over the capsule an open bell



jar, and quickly close it with a stopper. Note whether, in this case also, only a portion of the air is consumed, and whether in proportion it is approximately equal to that absorbed by the iron filings. Does the residual gas support the combustion of a taper? Observe the fumes of a white solid substance, which may be supposed to be to phosphorus what iron rust is to iron, *i.e.* the product of the absorption of the active constituent of the air. Observe also that

these fumes slowly dissolve in the water and render it acid, this being shown not only by its taste, but also by its power of changing the colour of a solution of litmus from blue to red, a characteristic property of acid liquids.

It will be noticed that the products of the rusting of iron and the burning of phosphorus are entirely different in properties from the iron, the phosphorus, and the gas of which they are composed. Iron rust is red in colour and devoid of metallic lustre, and will be found to be, unlike iron, not attracted by a magnet. The fumes from burning phosphorus are not inflammable and are soluble in water, forming an acid liquid. Nor has either substance any of the properties of the gaseous constituent that has been absorbed. It is obvious that the two constituents of each product have become united or combined together so intimately that the characteristic properties of each constituent have been entirely changed, the compounds having none of the properties that a mere mixture would possess.

From these experiments it must therefore be concluded that the air is not homogeneous, but consists of at least two gases mixed together—(1) an active gas—oxygen—constituting about one-fifth of the air, and (2) an inactive gas—nitrogen—constituting about four-fifths; and that when substances undergo changes due to atmospheric action, such as rusting and burning, chemical combination of the substance with the oxygen of the air occurs, chemical compounds being formed having properties entirely different from the original substances. These substances, if they be not themselves compounds, are termed elements. The compounds of oxygen may be called oxides. Thus, iron rust is oxide of iron, and the product of the combustion of phosphorus is oxide of phosphorus.

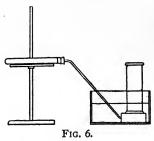
IV. OXYGEN GAS

THE nitrogen gas left behind when the oxygen has been removed from air by burning phosphorus or rusting iron is distinguished by its inability to support combustion or to promote rusting. It is now necessary to try to procure the oxygen gas of the air in the pure state, in order that its properties may also be studied.

The oxide of iron (iron rust) already produced contains oxygen derived from the air. Can the oxygen be obtained from it? Since heat decomposes many chemical compounds, such as the constituents of wood and coal with the production of gas, try heating some iron rust in a test-tube. Should no decomposition occur at the highest temperature obtainable, try heating the oxides of other metals, e.g. the black oxide of copper, the red oxide of mercury, and the red oxide of lead (red lead), all of which can be obtained by gently heating the

metals in air. Should one or more of these oxides yield up their oxygen, or a portion of it, on heating to a high temperature, a method will have been found of preparing the oxygen gas of the air in a pure state. A smouldering splint will indicate whether the gas is being evolved.

Heat some red lead or red oxide of mercury in a hard glass tube, fitted with a cork and bent tube, as shown in Fig. 6, supported on the ring of a retort stand, and collect the gas



evolved by allowing it to bubble up into an inverted test-tube or cylinder filled with water. When all the water has been displaced, and the tube is full of gas, place the thumb or a glass plate over the orifice while still under water; then turn up and examine the properties of the gas. In taste, odour, and colour it would be expected to be indis-

tinguishable from air, air being tasteless, odourless, and colourless, but, being the pure active constituent, it should support combustion more readily. Try with a taper and a smouldering splint.

Fill a bottle with oxygen (supplied) by water displacement, and having placed a bit of phosphorus in a deflagrating spoon, and set fire to it, plunge it into the bottle. Repeat the experi-



Fig. 7.

ment, using sulphur instead of phosphorus. Then try a lump of charcoal supported by a copper wire passing through the brass plate of the spoon. Finally, try a steel watch spring, to the end of which a bit of taper is fixed to serve as a fuse, the other end of the spring passing through the brass plate. Observe in each case that the oxygen is more active as a supporter of combustion than air, but that the product of combustion is the

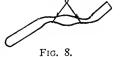
same. Carefully note the properties of these products, *i.e.* the oxides produced, with respect to appearance, odour, solubility, and, if soluble, acidity of the solution. Be careful to enter each observation in the notebook during the progress of the experiment.

It will be noticed that while heat caused the decomposition of the oxides of mercury and lead, heat was produced when phosphorus, sulphur, charcoal, and iron combined with oxygen. In subsequent experiments, note whether heat is invariably produced when chemical combination occurs. Again, heat appears to promote chemical change, for the oxides were only formed rapidly when the elements had been heated sufficiently to ignite them. Is this observation also general?

When iron rusts, increase of weight occurs because the oxygen of the air with which it combines also possesses weight. Is there any definite proportion between the weights of substances which combine together. Determine, for instance, whether red oxide of mercury contains definite proportions of mercury and oxygen.

Construct a hard glass tube as figured, using a blow-pipe for softening and working the glass, and weigh by suspending it to the arm of the balance by a piece of copper or, better, platinum

wire. Place in the bottom of the tube about five grams of red oxide of mercury, previously heated in the hot water oven to dry it, and weigh again. The difference will be the exact weight of



the oxide taken. Heat till the whole of the oxide has been decomposed, care being taken not to heat the upper portion of the tube, allow to cool, and weigh. The difference in weight between the mercury left and oxide of mercury taken will be the oxygen evolved. Calculate the amount of oxygen combined with 100 parts by weight of mercury. Repeat the experiment till concordant results are obtained.

Compare the result with the results obtained by other

students who, if possible, should use different specimens of the red oxide. Should they have found the same combining proportions, it must be concluded that mercury and oxygen combine in definite proportions by weight. Subsequent experiments will show whether this is true of the elements of other chemical compounds.

V. THE THIRD CONSTITUENT OF THE AIR

Besides rusting and burning, another familiar change that takes place in air is the conversion of lime into chalk. Expose some solution of lime ("lime water") in a beaker to the air. Note that in a few minutes it becomes covered with a white scum of chalk, chalk being distinguished from lime by being insoluble in pure water. Repeat the experiment, but use a stoppered bottle filled with air instead of an open beaker. Note that the amount of chalk now formed is extremely small, and that no appreciable absorption of the air in the bottle occurs. These experiments show that there is a constituent in the air which converts lime into chalk, but that it is present in very minute quantities, and that the oxygen and nitrogen of the air are not concerned in the change.

Since the product of combustion of charcoal or carbon—the oxide of carbon—is a gas, it is very probably a constituent of the air, and it may be this which converts lime into chalk. Burn some charcoal in a bottle of oxygen (supplied), and test the gas produced with lime water. Should chalk now be formed, this third constituent of the air will have been identified as the oxide of carbon.

Re-examine the properties of this gas as prepared by the combustion of charcoal in oxygen. Try whether it is able or unable to support the combustion of a taper. Leave a bottle of the gas open, and test it from time to time with a burning

taper. Note that the escape of the gas from the bottle is very slow, for it remains at the bottom like a liquid. Try to pour it from one bottle to another like water. Pour some water into a cylinder of the gas, and, having covered with a greased plate, shake vigorously. Now attempt to remove the plate, and note whether there is evidence of the gas being soluble. Test the liquid in the bottle with litmus solution, and note whether it is acid. These experiments show that the gas is unable to support combustion, heavier than air, and soluble in water forming an acid solution.

Air and Ventilation.-This oxide of carbon, usually known as carbonic acid gas, is a product of combustion, not only of charcoal, but of all ordinary fuels, solid, liquid, and gaseous, all of which contain combined This may be shown by burning a candle, a jet of coal gas, etc. in a bottle, closed at the top with a brass plate, until the flame expires, and then testing the contents of the bottle with lime water. Carbonic acid gas is also a product of animal respiration. If a jar of air expired from the lungs be collected over water, it will be found to render lime water milky, and to be so rich in carbonic acid gas and deficient in oxygen as to extinguish a lighted taper. The amount of carbonic acid gas normally present in air is not more than .03 or .04 per cent., and this small amount is not injurious to health. In the air of towns it may reach .06 per cent., and quantities in excess of this are held to be prejudicial to health. London air . I per cent, is sometimes observed, while in a crowded room it may reach .3 per cent. Air containing 3 per cent. extinguishes a lighted taper, while air containing 4 per cent. is fatal to life.

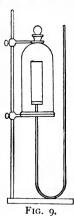
An adult breathes out about .6 cubic feet of carbonic acid gas per hour, while a jet of coal gas burning at the rate of 3 cubic feet per hour produces at least 1.4 cubic feet of carbonic acid gas. The carbonic acid gas in the air of a room having a capacity of 10,000 cubic feet, would therefore in one hour increase from .04 to .06 per cent. (the healthy limit) by the respiration of one man and combustion of one gas jet, if there were no ventilation. As vitality is reduced by breathing vitiated air, and the germs of disease flourish in a close and heated atmosphere, the efficient ventilation of dwelling-rooms and public buildings, as well as of sheds where farm stock are housed, is a matter of very great importance; and many instances are recorded of the spread of disease among human beings and among

cattle owing to want of ventilation.

Ventilation is effected by utilising three principles:-(1) Gases diffuse

into each other independently of their weight. If an inverted jar of coal gas, which is lighter than air, be placed over a jar of carbonic acid gas, heavier than air, the gases will be found in a few minutes' time completely mixed, as shown by the inflammability of the gas in each jar, and the milkiness it produces in lime water. It is due to this diffusion of gases that the carbonic acid gas does not settle on the floor of a room, and that, if apertures are provided, complete admixture with the outer air gradually takes place.

(2) Diffusion takes place through porous materials; the rate of diffusion of two gases is inversely as the square roots of their relative weights. This is best illustrated by the apparatus figured. A porous earthenware cell is



fitted with an india-rubber cork and glass U tube half filled with a coloured liquid. A bell jar filled with coal gas is placed over the cell. The lighter coal gas enters the cell more quickly than the heavier air escapes, and, in consequence of increased pressure in the cell, the red liquid is depressed. On now removing the bell jar. the coal gas escapes from the cell more quickly than the air enters, and, in consequence of the diminished pressure in the cell, the red liquid rises. Bricks, mortar, plaster, etc., are porous; iron and wood are non-porous. Brick walls provide better ventilation than walls of wood or corrugated iron, and whitewashed walls better than painted walls. The effect of diffusion is often well seen on a kitchen ceiling, where blackened strips between the beams show where air has diffused through, and black particles of soot and dust filtered out.

(3) Gases expand by heat, consequently become lighter and rise; air currents are thus produced. The best illustration of the expansion of gases by heat is

the air thermometer, the movement of the liquid in the stem indicating expansion or contraction of the air in the bulb, due to changes of tem-



Fig. 10.

perature. The air current thus produced may be illustrated by an aspirating bottle in which a candle is burning. The candle will shortly be extinguished unless the cork from the lower aperture is opened, thus giving rise to an air current

and ventilation. The modern contrivances for the ventilation of rooms have all for their object the admission of air and production of air currents without producing draught.

In what proportion are carbon and oxygen combined in carbonic acid gas? In order to determine this, charcoal is burnt in a hard glass tube in a current of oxygen.* The carbonic acid gas produced together with the excess of oxygen is passed through a solution of caustic potash, and finally through a tube containing lumps of caustic potash, this being a substance which, like lime, absorbs carbonic acid gas, but allows the excess of oxygen to escape. The tube containing the charcoal, and the bulbs and tube containing the caustic potash, are weighed before and after the experiment. The former gives the carbon consumed, the latter the carbonic acid gas produced; the difference between the two will be the oxygen combined with the carbon.

The following numbers were obtained from an experiment:—

From these figures calculate the proportion of carbon and oxygen per cent. of carbonic acid gas, and also calculate the

^{*} This experiment is too difficult for elementary students, and therefore only a bare outline of the method is given. It should, however, be performed by the teacher with the aid of his students. To ensure a correct result, the oxygen should be dried by passing through a U tube containing pumice soaked with oil of vitriol, the charcoal must be previously heated in a current of chlorine to eliminate every trace of hydrogen, and the products of combustion of the charcoal must be passed through a heated tube of oxide of copper, to ensure complete oxidation before passing into the solution of caustic potash which should be contained in properly constructed potash bulbs. Two or three experiments can be made with the same charcoal and potash, one after the other.

amount of carbon combining with 8 parts of oxygen (i.e. the amount which was found to combine with 100 of mercury). Numerous experiments have shown that carbonic acid gas invariably has a uniform composition; like mercury, carbon combines with oxygen in definite proportions by weight.

VI. AQUEOUS VAPOUR, WATER, AND ICE

Besides rusting and burning and the conversion of lime into chalk, another change that is often noticed taking place in the air is the *deliquescence* of certain substances, such as common salt and chloride of calcium. Place some of the latter in a covered dish and weigh, then expose to the air till partially liquid and weigh again. Should the substance now weigh more, it may be assumed that the liquefaction is due to the absorption of atmospheric moisture in which the chloride of calcium has dissolved. To confirm, heat the partially liquid substance in a test-tube, and notice whether moisture is given off and deposited on the sides of the tube. This change may be

observed even in the driest weather, showing that water vapour is always a constituent of the atmosphere.

Besides existing in the gaseous state, as water vapour or steam, and in the liquid state, water exists in the solid state as ice. The temperatures at which these changes of state take place are called the boiling and freezing points. Determine the boiling point of water by finding the temperature of the steam escaping from rapidly boiling water contained in a flask fitted with a cork, tube, and centigrade thermometer

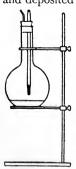


Fig. 11.

as figured. Continue the experiment till a constant reading is obtained.

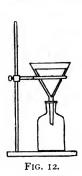
The temperature of boiling water depends upon the purity of the water, the temperature of the steam is constant; hence the latter is determined. A small flame without wire gauze is best for heating the water, otherwise the sides of the upper part of the flask are apt to become superheated. Since the recording of the temperature by the thermometer depends upon the expansion of the mercury by heat, the mercury in both bulb and stem must be in the steam. Water only boils when it is so hot that the pressure of the water vapour is able to overcome the pressure of the atmosphere. The boiling point, therefore, varies with the atmospheric pressure; and hence, when a boiling point is determined, the reading of the barometer must also be noted.

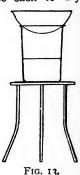
The boiling point of water is also the condensing point of steam; likewise, the freezing point of water is the melting point of ice. Determine the latter by immersing the end of a thermometer in a beaker filled with melting snow, or with finely powdered ice saturated with water. Constantly stirring the mixture with the thermometer, repeatedly note the temperature without removing the thermometer from the beaker till a constant reading is obtained.

The graduation of a thermometer is seldom quite correct, and future readings should always be corrected for any error thus found. On the centigrade scale, the freezing point is the zero ("o" C."), and the distance between that and the boiling point is divided into 100 degrees. On the Fahrenheit scale, the freezing point is 32 degrees above the zero, and the distance between this and the boiling point is 180 degrees, the boiling point being "212" F." Each degree Fahrenheit is therefore $\frac{100}{180}$ of a degree centigrade. Compare the reading of a centigrade and Fahrenheit thermometer. Do they record the same temperature?

VII. WATER AS A SOLVENT

SHAKE some common salt, gypsum, and sand separately with pure water, filter the liquids, from undissolved substance, through a cone of porous paper fitted in a funnel as figured, into porcelain basins, and evaporate each to dryness over





beakers of boiling water (Fig. 13). Judging from the residue, which substance would be described as insoluble, which as slightly soluble, and which as very soluble in water?

Determine the solubility of gypsum. Stir excess of pure gypsum with pure water (at 15° C.) in a beaker until, after prolonged stirring, a saturated solution is obtained. Then filter and evaporate 25 grams of the filtrate in a weighed porcelain basin to dryness on the water bath. Weigh the dish and residue. Calculate the amount of gypsum dissolved by 1 gram of water (the "co-efficient of solubility" of gypsum). Repeat the experiment until concordant results are obtained.

The solubility of a solid in water usually increases with rise in temperature, for heat tends to promote change from the solid to the liquid state. It is therefore necessary to adopt a standard temperature in the determination of solubilities. The usual temperature of the laboratories is 15° C., and this is therefore generally adopted.

Liquids and gases, like solids, vary in their solubility in water. Compare the solubility of alcohol, chloroform, and paraffin oil by shaking the liquids, added drop by drop, in large test-tubes of water. Compare the solubility of carbonic acid gas (supplied) and air by inverting test-tubes of the gases in recently boiled and cooled water, and noting the height to which the water rises in the tubes. Since heat tends to promote change from the liquid to the gaseous state, it is to be expected that a gas will be more soluble in cold than in hot water. Heat some rain water in a test-tube, and note that, as the temperature rises, bubbles of gas are given off.

The foregoing experiments indicate a method of obtaining perfectly pure water by *distillation*; for on boiling water, the dissolved gases are first evolved, the dissolved solids are left behind, and the steam is pure water vapour which can be condensed to pure water. Distil some water in a retort, and

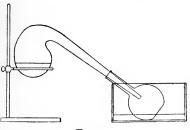


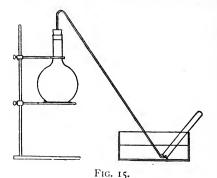
FIG. 14.

lead the steam into a flask kept cold by a trough of cold water, in order that the temperature may be reduced below the condensing point of steam. Reject the first part of the distillate, and collect that which comes over afterwards. Note that the dissolved solids are left as a residue in the retort.

Rain, Spring, and Sea Water.—Water exercises an appreciable vapour pressure at all temperatures, and this increases as the temperature rises, until at the boiling point it is equal to the atmospheric pressure. It is

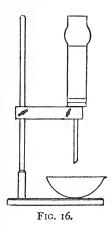
due to this that evaporation of water takes place much more rapidly in hot weather than in cold, and that warm air can absorb much more water vapour than cold air before it becomes saturated. The amount of water vapour that can be retained by air, therefore, depends upon the temperature. Water vapour is always present, and however apparently dry the air may be, a temperature is reached on cooling-the "dew-point"-at which water vapour begins to condense in the form of mist or dew. This temperature is most easily determined by the dew-point hygrometer, but it can also be ascertained by calculation from the difference between a wet and a dry bulb thermometer. These thermometers will record the same temperature when the air is saturated, but the drier the air is the more will the reading of the wet bulb fall below that of the dry, because greater evaporation from the wet bulb takes place, and more heat is absorbed in consequence (see p. 34). The deposition of dew when air is cooled is conveniently illustrated by bringing a flask of ice-cold water into a warm room.

The distillation of water that occurs in nature will now be understood. Air into which water has evaporated from sea and land deposits its water when cooled in the form of cloud, mist, or dew. From cloud, water is precipitated as rain; so that rain is distilled water, free from all dissolved solids, and only containing the dissolved oxygen, nitrogen, and carbonic acid gas of the atmosphere. These gases may be obtained for examination by completely filling an apparatus, such as that figured, with rain water,



and heating the flask until the gases are expelled. When rain water sinks through the soil and the underlying strata, it dissolves the soluble substances; so that river and spring water contain dissolved solids varying in

their character and quantity according to the soil and rock strata through which the water has passed. Such water ultimately finds its way to the sea, and there again undergoes evaporation, leaving the solids behind either



dissolved or deposited, so that the sea is the liquid residue of ages of evaporation. The action of rain water as a solvent on soil may be illustrated by percolating soil with rain water in the apparatus figured, and comparing the residues of evaporation of the rain and drainage water.

VIII. DENSITY

It is well known that salt water is more buoyant than pure water. This is owing to its greater density. Compare the densities of water and a saturated solution of salt by comparing the weights of equal volumes of the liquids. Run 20 c.c. of the salt solution from a burette into a small

weighed flask and weigh. Subtract the weight of the flask to obtain the weight of the salt solution. Since 20 c.c. of



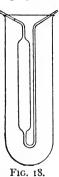
FIG. 17.

water (at 15° C., see page 13) as run from the burette will weigh 20 grams, the relative weights of equal volumes of the salt solution and water can thus be ascertained. the density of water as 1, what is the relative density of the salt solution?

The density of a solid or liquid is always compared with water as unity. The number thus obtained is the relative density (or specific gravity) of the substance. A customary method for taking specific gravities is by

the specific gravity bottle, constructed to hold exactly 50 or 100 grams of water at 15° C. (Fig. 17). An improvement on this method is described in the next paragraph.

In repeating the determination to obtain concordant results employ a U tube (Fig. 18), by the use of which the tempera-



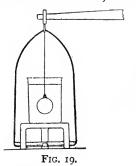
ture of the liquid can be controlled. Construct such a tube out of a piece of soft glass tubing having a 5 or 6 m.m. bore, and weigh it. Now fill with water by attaching an india-rubber tube and sucking up the water through the drawn-out Having removed the india-rubber tube, end. the drawn-out end of the U tube should remain filled with water, while the water in the other end will sink to a certain point. Mark this point with a file. Immerse the tube in a beaker of water at 15° C. for a few minutes: then, if necessary, run a little water in, or suck a little out by pressing a bit of filter paper to

the drawn-out end, until the height of the water in the one limb exactly coincides with the mark when the tube is quite upright, and, having dried the outside of the tube, weigh. Empty the tube, and having first rinsed it out with the salt solution, fill it with the solution; when it stands at the mark after suspending in the beaker of water at 15° C. for a few minutes, dry and weigh.

Like liquids, solids differ in their density. Wood floats on water, but iron sinks. Compare the densities of glass and water. Weigh a piece of stout glass rod. Immerse it in the water in a half-filled burette, and read off the increase in the height of the water. The increase will be an amount of water equal in volume to the glass rod. From this calculate the relative density of the glass.

Solids weigh less when immersed in water than in air; the

loss in weight is found to be equal to the weight of water displaced. Weigh the glass rod under water, by suspending it to the arm of the balance by a hair, as figured. The loss in weight will be found to be equal to the weight of water it displaced, as found in the previous experiment. This provides an exact method for determining the relative density of solids. Weigh the solid first in air and then in water, and



compare its weight in air with the loss in weight, i.e. the weight of an equal volume of water.

It is obvious that the loss in weight of a solid when immersed in a liquid will depend upon the density of the liquid, for the loss in weight is equal to the weight of an equal volume of the liquid. Hence this method also provides a means of determining the density of liquids. For example, to determine the relative density of the salt solution, compare the loss in weight of the glass rod when immersed in the salt solution with its loss in weight when immersed in water, *i.e.* the weight of equal volumes of salt solution and water.

This principle is adopted in the rough determination of

relative densities by means of the hydrometer. This is an instrument constructed to float upright in a liquid, and which records the relative density of the liquid by the depth to which it sinks, the stem being graduated in "degrees of specific gravity," water being taken as 1000. The liquid must be at 15° C. Compare the relative density of the salt solution as determined by the hydrometer with that determined by the previous methods.

Other Properties of Water.-Water has a great heat capacity. If beakers of water and mercury be placed side by side in a bath of hot water, the mercury will become hot much sooner than the water, and, when both are hot, the water will remain hot much longer. Water has also a greater heat capacity than the constituents of rocks and soil. If into each of two beakers, the one containing a pound of cold water and the other a pound of sand, a pound of boiling water be poured, and each stirred with a thermometer, the temperature of the mixture of sand and water will be found to be the higher, the heat capacity of the sand being less than the water, and requiring less heat to heat it than the cold water. The heat that would raise I lb. of water I°C. would raise 5 lbs. of sand I°, and would raise I lb. of sand 5°. The relative or specific heat capacity of sand is therefore .2 (water = 1). Water is taken as the standard, as it has the greatest heat capacity of all ordinary solid or liquid substances. partly for this reason that Great Britain, being surrounded by water, has so temperate a climate, because the sea absorbs more heat in summer and gives up more heat in winter than land. For the same reason a dry, sandy soil is "warmer" than a clay soil, because the latter retains so large a quantity of water.

When change of state occurs from a solid to a liquid, or a liquid to a gas, heat is absorbed. Since heat is again produced when these changes of state are reversed, it is spoken of as the *latent heat* of liquefaction, and the *latent heat* of vaporisation. An example of the latter is seen in the wet and dry bulb thermometers. The wet bulb thermometer will read the lower, unless the air be saturated with water vapour, because the evaporation from the surface is accompanied by absorption of heat. An example of the former is the freezing mixture produced by mixing salt and snow. The salt produces rapid melting of the snow, and heat is consequently absorbed, the temperature falling to -21° C. The loss of heat by the great evaporation from the sea during the summer is another cause of the temperate character of the climate of Great Britain. For this reason

also, a sandy soil is "warmer" than a clay soil, and a room with damp walls is chilly.

Water vapour is an athermanous gas, i.e. it does not readily allow the radiation of heat through it, unlike the other gases of the atmosphere, which are diathermanous. The atmosphere of Great Britain being humid, the intensity of the sun's heat in summer, and the radiation of the earth's heat into space in winter, is less than in drier countries in the same latitude, and the climate is consequently more temperate.

Water contracts when it cools from 100° to 4° C., but, unlike other liquids, expands from 4° to 0°, and, on freezing, further expands to the extent of 9 per cent. of its volume. These changes may be studied by filling a large thermometer tube and bulb with hot water (Fig. 10), and gradually cooling to a temperature below the freezing point. They explain the necessity for observing the temperature in calibrating burettes (p. 12), and in determining the density of solids and liquids (p. 31). They are of importance (1) in the production of ocean currents, another factor having a great influence on the climate of Great Britain; (2) in the preservation of animal life in lakes and ponds; (3) in the rupture and decay of vegetable tissue; (4) in the heating of buildings by hot water; (5) in the bursting of water pipes during frost; and (6) in the disintegration of rocks and soil by frost.

The physical properties of water are compared with those of mercury and alcohol in the following table.

PHYSICAL PROPERTIES OF LIQUIDS.

	Water.	Mercury.	Alcohol.
Specific gravity Specific heat (at 15°)	1.000 at 4°	13.596 ⁰ ° 0.033	0.794 ^{15°} 0.612
Latent heat of fusion, in heat units Latent heat of vaporisation,	79.25	2.82	3
in heat units Boiling point (at 760 m.m.) Freezing point	535.77 100° 0°	62.00 357° -38.5°	208.92 78.4° -130.5°
Vapour pressure at 15° in mm. of mercury Co-efficient of expansion	12.67	0.04	32.44
from o° to 100° Thermal conductivity .	0.00043 0.083	0.00018 0.925	0.00127 0.029

IX. COMPOSITION OF WATER

Is water an element or a compound, and if the latter, what are its constituents? To answer this question an attempt must be made to decompose it. The effect of heat, however, which has been found to decompose certain chemical compounds, is simply to change its state from water to steam. No chemical change occurs similar to that which resulted from heating oxide of mercury, for in this, and in all the other chemical changes studied, substances have been formed having entirely different properties from the original substances, and the changes are permanent and not simply changes of state. Possibly, however, steam, like air, can act chemically on iron, charcoal, etc., especially if these be heated to promote the chemical change:

Fit up the apparatus figured, and place in the wide tube, which must be constructed of hard glass, some iron filings

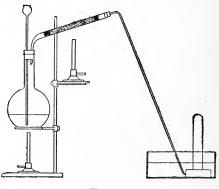
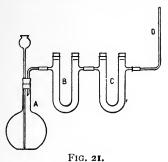


FIG. 20

(or, better, some iron turnings). Heat the filings to a low red heat; pass steam from the flask of boiling water very slowly through the tube, and lead the escaping gas or vapour into a trough of water. Note whether the iron filings become changed in appearance. Note, also, whether the escaping gas condenses in the water of the trough like steam, or whether it is a permanent gas. If the latter, collect some in an inverted tube of water, and study its properties. Is it a supporter or non-supporter of combustion, and is it combustible? Is the change in the iron due to its having combined with one element of the water, the other element, which from its source might be termed "hydrogen"—i.e. water producing—gas, being liberated? If so, water is a compound of this hydrogen with the element with which the iron has confbined. If—

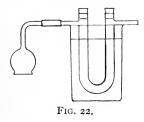
water + iron = (iron + x) + hydrogen, water = hydrogen + x.

The iron compound exactly resembles that which is obtained by heating iron in air, and it may therefore be an oxide of iron. If so, water must be oxide of hydrogen. An easy method of testing this supposition will be to burn hydrogen in air, when—since combustion in air consists in combination with the oxygen—water should be formed. For this purpose,



prepare some hydrogen gas in the apparatus figured, by pouring cold dilute sulphuric acid (1 of acid to 6 of water) through the thistle funnel on to some granulated zinc placed in the flask A.

To purify the gas thus obtained, pass it through the U tube, B, filled with pieces of pumice soaked with solution of potash (1 gram of caustic potash dissolved in 3 c.c. of water); and to dry it, through the U tube, C, filled with lumps of calcium



chloride. When all the air has been expelled from the apparatus, and pure hydrogen issues from D, ignite the gas, and, by means of an aspirator, draw the products of combustion through a small thistle funnel into a U tube half immersed in cold water (Fig. 22). Is the liquid, which condenses in the U

tube, water? Has it the physical properties of water? To answer this question, run it into a small flask, fitted with a thermometer, and having an aperture to allow steam to escape, and determine its boiling point. If this be 100° C., it is water. Water must therefore be the oxide of hydrogen.

Hydrogen and air form a dangerously explosive mixture. To ensure absence of air from the gas before lighting it at the jet, collect a test-tube by upward displacement of air, and ignite it. If air is still present, an explosion will be produced; if the gas is pure, it will burn quietly.

X. HYDROGEN GAS

It has been found that hydrogen differs from oxygen, nitrogen, and carbonic acid gas, in being combustible. It is also lighter in weight, for it has been possible to collect it by upward displacement of air. Compare its density with that of air. The density of gases may be compared, like liquids, by weighing equal volumes. Attach the flask (Fig. 1) to the

hydrogen apparatus, in such a way that the purified gas is led into the top of the flask while the air is driven out from the bottom. When every trace of air has been expelled, and it is completely filled with the hydrogen, detach the flask, stopper and weigh it. Now, by means of an aspirator, draw air, dried by slowly passing through the calcium chloride tube, into the flask the reverse way, until all the hydrogen has been driven out; detach, stopper, and weigh again. Next find the capacity of the flask by filling the flask and tubes with water and measuring the water. At 15° C., the temperature at which both the air and hydrogen should be, and when the barometer stands at 30 inches, 1000 c.c. of dry air weighs 1.226 grams. this calculate the weight of air in the flask, and subtract it from the weight of the flask filled with air, in order to determine the weight of the flask. The weight of hydrogen can now be determined by subtracting the weight of the flask from the weight of the flask and hydrogen. The weights of equal volumes of air and hydrogen being now found, calculate the relative density of air, taking hydrogen as 1, and that of hydrogen, taking air as 1. Repeat the determination until concordant results are obtained.

In the foregoing experiment great care must be taken completely to fill the flask with the gas. Until stoppered the flask must on no account be touched with the hands, as this would warm and expand the gas. The following example will serve to illustrate the method of working:—

Capacity of the flask = 1000 c.c.

1000 c.c. of dry air at 15° C. and 760 m.m. pressure weighs 1.226 grams.

Weight of flask and air = 101.226 grams. Weight of air = 1.226 ...

Weight of flask = 100.000

Weight of flask of hydrogen = 100.085 grams.

Weight of flask = 100.000 ,,

Weight of hydrogen = 0.085 ,,

Hence if air = 1, the relative density of hydrogen = .069, and if

hydrogen = 1, the relative density of air = 14.4. Hydrogen, being the

lightest gas known, is usually taken as unity.

When heated, gases expand much more than liquids or solids, and, unlike liquids and solids, they all expand equally and also regularly for each increment of temperature. On heating from 0° to 1° C., a gas expands $\frac{1}{2\sqrt{13}}$ of its volume, from 1° to 2° $\frac{1}{2\sqrt{14}}$, and so on. Thus 273 c.c. of air at 0° become 288 c.c. at 15°; 288 c.c. at 15° become 283 c.c. at 10°. The necessity for knowing the temperature in calculating the weight of air, and for having the hydrogen and air at the same temperature in the foregoing experiment, will now be understood; and should the temperature not be at

15°, it will be possible to calculate the weight of air in the flask

at any other temperature.

Gases are far more elastic and compressible than liquids and solids. The volume of any gas varies inversely with the pressure put upon it. Thus 1000 c.c. of air under a pressure of 30 inches of mercury become 1500 c.c. under 20 inches. This may be illustrated by means of the tube figured. If a little mercury at the bottom of the tube stand at the same level in both limbs, the air in the closed limb will be at the atmospheric pressure (say 30 inches of mercury). If now mercury be poured into the tube until it stands 30 inches higher in the long limb than in the short, the pressure upon the air in the short limb will be doubled, and the volume will be found to be reduced to half. If another 30 inches of mercury be added the pressure will be trebled, and the volume of gas reduced to onethird. In the foregoing experiment it is obviously necessary to take the barometric pressure into account, and should the barometer not stand at 30 inches, it is possible to calculate the weight of 1000 c.c. of air under any other pressure.

FIG. 23.

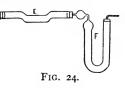
In what proportion does hydrogen unite with oxygen to form water? This may be determined by finding the quantity of water formed by the action of hydrogen on a known weight of heated oxide of copper, when the following change occurs:—

Hydrogen + oxide of copper = copper + oxide of hydrogen.

Fit up the apparatus figured. In the hard glass tube E place some oxide of copper. Heat the tube to a low red heat, and draw a current of air through the apparatus till every trace of moisture has been driven off; allow to cool; plug the holes

in the corks with little stoppers made of glass tubing, and weigh. Fill the tube F with lumps of chloride of calcium and weigh. Connect the tubes and attach

E to the U tube C of the freshly charged hydrogen apparatus (Fig. 21). When the whole apparatus is free from air and completely filled with pure hydrogen slowly passing through, heat the tube E till a portion of



the oxide of copper has been decomposed. Allow the tube to cool, and when every trace of moisture has been carried forward by the current of hydrogen into tube F, detach the tubes E and F, plug and weigh them separately. The loss in weight of E will be the weight of oxygen used. The gain in weight of F will be the weight of water produced. The difference between the weight of water produced and oxygen used will be the weight of hydrogen used. Calculate the percentage composition of water, and from that the quantity of hydrogen, combining with 8 parts by weight of oxygen, *i.e.* the combining weight of oxygen up to the present taken.

In repeating the determination to obtain a concordant result, use the same tube of copper oxide, care being taken that no damp air gains access to it, copper oxide being a very hygroscopic substance. If necessary reoxidise the copper by passing air through the heated tube. If more dilute sulphuric acid is required during the progress of the experiment, pour in a few drops at a time down the side of the funnel tube, so that no air, which would, of course, be fatal to a correct result, be admitted.

XI. CONCLUSIONS

THE foregoing studies in natural science are of two kinds:—

(1) Those which have reference to the properties of the

substances dealt with are *physical*, and (2) those which have reference to their *composition* are *chemical*. The systematised knowledge obtained by a study of the properties of matter constitutes the science of *Physics*; that obtained by a study of its composition constitutes the science of *Chemistry*. The changes observed which have involved alteration in composition, such as the rusting of iron, are chemical changes; those which have not necessarily involved any alteration in composition, such as the change of state of water to steam, are physical changes.

The chemical changes are of two kinds:-Those which are concerned with the decomposition of compounds into simpler compounds or into elements, such as the change produced by heating oxide of mercury, and those which are concerned with combination and the formation of compounds, such as the combustion of phosphorus. Very often a chemical change involves both chemical decomposition and combination, as in the action of steam on heated iron filings. It has been noticed that chemical change is promoted by heat, but that whereas chemical combination is accompanied by production of heat, it has been necessary to put back heat into a substance to decompose it. It is easily conceivable that if, owing to a force of chemical attraction between two elements, heat is produced when they unite, it would be necessary to employ a force, such as heat, capable of overcoming this attraction, to decompose a chemical compound.

Two methods are therefore available for investigating the composition of matter:—(1) Analysis, i.e. splitting up the compound in order to obtain its constituents; (2) Synthesis, i.e. putting together the constituents in order to obtain the compound. The composition of red oxide of mercury was found by analysis, that of carbonic acid gas by synthesis.

These investigations have shown that chemical combination takes place in definite proportions by weight. With 8 parts by weight of oxygen, 1 of hydrogen, 3 of carbon, and 100 of

mercury were found to combine to form water, carbonic acid gas, and red oxide of mercury. In the second part of these studies an inquiry will be made into the proportions in which other elements combine.

It has been observed that when hydrogen and oxygen combine they do so in definite proportions, a liquid—water—is formed, the properties of which are entirely and permanently different from the component gases, and heat is produced. These three characteristics of chemical combination show that water is a chemical compound. Air consists of oxygen, nitrogen, carbonic acid gas, and water vapour in variable proportions. If these gases be mixed together no heat is produced, but the mixture has the same properties as air. Air has therefore none of the characteristics of a chemical compound, and is merely a mixture.

For identifying chemical substances, both physical and chemical methods are available. Thus, the co-efficient of solubility of gypsum, the boiling point and freezing point of water, and the relative density of hydrogen gas are "physical constants" which are available for identifying these three substances. By chemical methods red oxide of mercury could be distinguished from red lead, as they behave differently on heating, and nitrogen from carbonic acid gas, as they differ in their action upon lime water and litmus.

QUESTIONS AND PROBLEMS FOR REVISION AND EXAMINATION.

The problems marked with an asterisk (*) are intended for practical examination.

WEIGHTS AND MEASURES.

- 1. Express 2195.817 grams in kilograms, hectograms, etc.
- Express I hectogram, 6 grams, 4 centigrams, and 9 milligrams in grams.
- 3. Calculate the number of milligrams in a kilogram.

4. Express 30 inches in millimeters.

5. What is the weight of 10 liters of pure water at 4° C.?

*6. Calibrate the burette.

THE ATMOSPHERE.

7. Describe how the weight of a liter of air can be ascertained.

8. To what is the atmospheric pressure due, and how may it be proved that the height of the mercury in a barometric tube depends upon the atmospheric pressure?

 Mercury is 13½ times as heavy as water. Calculate the pressure of the atmosphere upon the surface of the earth at sea level in grams

per square centimeter, and in lbs. per square inch.

10. Mercury is 11,000 times as heavy as air at sea level; what would be the height of the atmosphere in miles, were the density the same

throughout?

11. The action of a suction pump in drawing water depends upon the atmospheric pressure. Calculate the height to which it would be theoretically possible to draw water, were the water absolutely pure and the valves of the pump air-tight.

*12. The daily barometric readings for March 1898 were—30.5, 30.6, 30.4, 30.3, 30.0, 30.4, 29.9, 29.6, 28.8, 29.7, 29.2, 29.7, 30.0, 30.0, 30.0, 29.8, 29.8, 29.1, 29.1, 29.3, 28.8, 29.5, 29.5, 29.3, 29.6, 29.9, 30.1, 30.2, 30.2, 30.3. Express these variations graphically on the square paper.

COMPOSITION OF AIR.

13. Name the active and the inactive constituents of the air, and state in what proportion they are present.

14. When iron rusts under a bell jar standing over water, what changes take place in (1) the weight and properties of the iron, and (2) the volume and properties of the air?

15. When phosphorus burns, what happens to the phosphorus and to the air? In what respects is the combustion of phosphorus similar to

the rusting of iron?

16. What is an oxide? How may the oxides of iron and phosphorus be formed?

17. What is a chemical compound, and how would a chemical compound of two elements be distinguished from a mixture? Illustrate your answer by the compounds of oxygen with iron and phosphorus.

*18. Prepare a bottle full of nitrogen gas.

OXYGEN GAS.

- 19. Of the red oxides of iron, lead and mercury and the black oxide of copper, which yield oxygen on heating, and what are the residues left when oxygen ceases to be evolved?
- 20. Fully describe a method for preparing a bottle of pure oxygen gas. Illustrate your description by a drawing of the apparatus used.
- 21. Compare the properties of oxygen and nitrogen.
- 22. Describe the combustion of phosphorus, sulphur, charcoal, and iron in oxygen gas. Of each product describe the appearance and smell. Is it a solid or a gas? Is it soluble in water and is the solution acid in reaction?
- 23. Judging from the examples dealt with so far, what appears to be the relation of heat towards (1) chemical change in general, (2) chemical combination, and (3) chemical decomposition?
- 24. Describe minutely how the composition of red oxide of mercury by weight may be determined, and state the amount of oxygen existing in this compound combined with 100 grams of mercury.
- *25. Identify the metallic oxide (red oxide of iron, red oxide of mercury or red lead).
- *26. Prepare a bottle full of oxygen gas.

CARBONIC ACID GAS.

- 27. In what proportion does carbonic acid gas exist in the air? How may its presence be demonstrated, and to what is it due?
- 28. Describe a method for preparing carbonic acid gas.
- 29. Give the properties of the gas. Does it support combustion? Is it soluble in water, and if so, what is the action of the solution on litmus? Is the gas heavier or lighter than air, and how does it behave to lime water and solution of potash?
- 30. Fully describe the method of determining the composition of carbonic acid gas, and state in what proportions carbon and oxygen are combined in this compound.
- 31. Why should the ventilation of rooms be necessary? In your reply state to what the vitiation of air is due, to what extent may the composition of air in rooms be altered, and what is the effect upon the health of breathing vitiated air.
- 32. State what you know about the diffusion of gases. How may this principle be utilised in ventilation?
- 33. What is the effect of heat upon the volume of a gas, and how may this effect be utilised in promoting ventilation?
- *34. Identify the gas (oxygen, nitrogen, carbonic acid gas, or air).

AQUEOUS VAPOUR, WATER, AND ICE.

- 35. What is meant by "deliquescence," and to what is it due? Name two substances that commonly exhibit this phenomenon.
- 36. What are the "three states of matter," and what is meant by "change of state"?
- 37. What do you understand by "temperature"? Name the instrument used for measuring temperature, and describe its construction and action. Why can water not be employed instead of mercury or alcohol in its construction? (See Study VIII.)

38. What is meant by the "boiling point" and "freezing point"? Why, in the determination of the former, must the atmospheric pressure

be taken into account?

39. Into what number of degrees are the Fahrenheit and centigrade scales of temperature divided, and what is taken as the zero for each scale? What fraction of a degree centigrade is a degree Fahrenheit? Calculate 15° C. into degrees Fahrenheit, and 20° F. into degrees centigrade.

*40. Determine the boiling point of the liquid.

*41. Is the zero point of the centigrade thermometer correct?

WATER AS A SOLVENT.

42. What is meant by the terms solubility and insolubility? Illustrate your answer by examples of solids, liquids, and gases. When is a solution said to be saturated?

43. What is the usual effect of rise in temperature upon the solubility of (1) a solid, (2) a gas? Trace the relation between this and the effect of temperature upon change of state of solids and gases.

44. Explain distillation with reference to change of state. How may distillation be employed to produce pure water from water containing solid and gaseous impurities?

45. Why does evaporation of water take place at temperatures below the boiling point? Will evaporation from the soil take place more rapidly in dry weather or damp, warm weather or cold?

46. If the air be saturated with water vapour, what takes place if the temperature falls? What is meant by the "dew point"? Why does the wet bulb thermometer read lower than the dry except when the air is saturated with water vapour?

47. Give an account of the distillation of water that takes place in nature; trace the history of water from the point at which it is evaporated from land or sea, through its existence as rain, spring, river, and sea water, with especial reference to the gaseous and solid substances it dissolves.

- *48. Determine the co-efficient of solubility of pure salt at 15° C.
- *49. Determine the percentage volume of gas evolved by boiling the tap water.
- *50. Determine the percentage of total solids in the tap water.
- *51. Percolate 100 grams of the soil with distilled water, previously boiled and cooled, until completely exhausted, and determine the percentage of soluble matter in the soil.

DENSITY.

- 52. What is meant by "density," and how may it be expressed? What is meant by saying that the "relative density" or specific gravity of brine (saturated at 15° C.) is 1.207?
- 53. A bottle holds 28.35 grams of water and 29.30 grams of milk at the same temperature. What is the specific gravity of the milk?
- 54. Twenty-five c.c. of a liquid weigh 30.5 grams. What is its relative density?
- 55. A piece of glass weighing 25 grams displaces 10 c.c. of water (at 4° C.).

 What is the relative density of the glass?
- 56. To what extent does a solid lose weight when immersed in a liquid? If the density of the solid be less than the density of the liquid, will it float or sink? Try to explain why.
- 57. A piece of hard glass weighs 27 grams in air, 16 grams in water, and 11 grams in brine. What is the relative density of the glass and of the brine?
- 58. Fully describe the construction of the hydrometer. How can it be employed for the determination of the relative density of a liquid, and why must the temperature of the liquid be ascertained?
- *59. Determine the relative density of the liquid by means of a U tube (at \(\frac{15}{5}\)).
- *60. Determine the relative density of the glass, and then, by means of the glass, that of the spirit.

OTHER PROPERTIES OF WATER.

- 61. What is meant by "heat capacity"? Name the substance which has the highest heat capacity of all ordinary solids or liquids. If beakers of water and oil were heated equally, which would become hot the quicker? When both are hot, which would cool the quicker?
- 62. If I lb. of boiling water be poured into I lb. of water at 15°, the temperature of the mixture is found to be 57.5°. If I lb. of boiling water be poured into I lb. of sand at 15°, the temperature of the mixture is found to be 86°. What is the heat capacity of the sand compared with that of water as unity?

63. Point out how the great heat capacity of water renders (1) the climate of Great Britain temperate, (2) a wet soil cold, and (3) a damp room chilly.

64. Point out the relation of heat to change of state, both from a liquid to a solid and a gas, and from a solid and a gas to a liquid. Explain the difference of temperature exhibited by a wet and dry bulb thermometer. Why does a mixture of salt and snow act as a freezing mixture?

65. Point out how the high latent heat of vaporisation possessed by water helps to render (1) the climate of Great Britain temperate, (2) a wet soil cold, and (3) a damp room chilly. Explain why the high latent heat of liquefaction of ice gives rise to a raw, cold feeling during a thaw.

66. What is meant by the terms "athermanous" and "diathermanous"? How does the athermancy of water vapour affect the climate of Great Britain?

67. Describe the effect of heating and cooling water upon its volume. Point out how these changes in volume can be utilised in the heating of buildings. It is stated that the water in a deep pond whose surface is frozen rarely sinks below 4° C. Explain this. Account for the useful effect of a hard frost upon the soil.

68. Compare the use of alcohol and mercury in the construction of thermometers, taking into account their difference in specific heat, boiling point, freezing point, co-efficient of expansion, and thermal

conductivity.

COMPOSITION OF WATER.

69. Describe fully the experiments which showed that water was a compound of hydrogen. State what change took place in (1) the iron filings, (2) the steam.

70. Describe the experiment which established the composition of water by synthesis, and state how the liquid produced was identified as

water

71. Before a jet of hydrogen is ignited, what precaution must be taken to ensure its purity? Why should hydrogen and air constitute an explosive mixture?

72. What do you mean by a "permanent" gas?

73. Two methods have now been employed to decompose chemical compounds. What are they? Illustrate your answer by examples.

*74. Identify the two gases (hydrogen, and either oxygen, nitrogen, or carbonic acid gas).

HYDROGEN GAS.

75. Describe two methods for preparing hydrogen gas.

76. Compare the properties of hydrogen, in respect to combustibility, smell, colour, solubility and density, with oxygen, nitrogen, and carbonic acid gas.

77. Give an account of the method for determining the relative density of

hydrogen

78. Calculate the relative density of a gas (hydrogen = 1) from the following data:—

Capacity of flask = 980 c.c.

Weight of flask and air at 15° C. and 760 m.m. = 88.303.

Weight of flask and gas at the same temperature and pressure = 88.407.

A liter of air at 15° C. and 760 m.m. weighs 1.226 grams.

The relative density of hydrogen (air = 1) is .069.

79. To what extent do gases expand when heated? What would 10 c.c. of a gas at 0° C. measure at 100° C., and what would 15 c.c of a gas at 15° C. measure at - 5° C.?

80. To what extent do gases expand or contract under variations of pressure? What would a liter of air under the normal atmospheric pressure measure under a pressure of 90 inches of mercury (3 atmospheres)?

81. What weight of air would a liter flask hold at a temperature of 20° C.

and a pressure of 29 inches of mercury?

82. Give an account of the determination of the composition of water by weight, and illustrate by a drawing the apparatus used. Refer especially to all the precautions that must be taken to obtain a correct result.

*83. Prepare a bottle full of pure hydrogen gas.

Conclusions.

84. Distinguish between the sciences of physics and chemistry. Give examples of physical and chemical change.

85. Distinguish between the two kinds of chemical change, and illustrate each kind by examples. Point out how in the action of steam on heated iron, and of hydrogen on heated copper oxide, both kinds of chemical change take place simultaneously.

86. Discuss the relation of heat to chemical change.

87. What are the two available methods for investigating the composition of matter?

88. What are the three characteristics of chemical combination? Why do we regard water as a chemical compound, and air as a mere mixture of the constituent gases?

89. In what proportions do mercury, carbon, and hydrogen combine with oxygen to form red oxide of mercury, carbonic acid gas, and

water respectively?

90. For identifying chemical substances we can employ both physical and chemical methods. Give illustrations of each.

PART II

XII. BASIC OXIDES, ACID OXIDES, AND SALTS

In studying air and water, it has been found that oxygen forms an important constituent of each. This is also true of the crust of the earth. The older rocks, such as granite; the stratified rocks formed by the disintegration of the older rocks, such as limestone or chalk, clay and sand; and soil formed by the disintegration and mixture of the foregoing, almost entirely consist of oxygen compounds. It is therefore necessary in commencing a study of the constituents of the earth's crust to examine the oxides more closely.

It has already been observed that certain oxides are soluble in water, and that their solutions have acid properties; for they are sour in taste and turn blue litmus red. Prepare the oxides of phosphorus and sulphur by burning the elements in jars filled with air or oxygen (Fig. 7), and containing a little water to dissolve the fumes of the oxides produced. Prepare the oxides of the metals magnesium and potassium by heating in the air (the latter in an iron spoon) till ignited. Dissolve the oxide of potassium in water and filter the solution. Mix the oxide of magnesium with a few drops of water in a dish, it being only very slightly soluble. Compare the action of the four liquids on blue and red litmus paper. Do they turn blue litmus red or red litmus blue? Are they acid or alkaline in reaction?

It will be found that of these four oxides, two dissolve in water forming acid, two dissolve forming alkaline liquids. The

two alkali-forming or basic oxides were oxides of metals, the two acid-forming or acidic oxides were oxides of elements which, not being metallic, may be termed non-metals. Similarly, other oxides will be found to be basic or acidic according to the metallic or non-metallic nature of their respective elements. Thus the more important oxides may be classified as follows:—

METALLIC OR BASIC OXIDES.

Oxide of aluminium (alumina).
Oxide of barium (baryta).
Oxide of calcium (lime).
Oxide of copper.
Oxide of iron.
Oxide of lead (litharge).

Oxide of magnesium (magnesia).
Oxide of manganese.
Oxide of mercury.
Oxide of potassium (potash).
Oxide of sodium (soda).

Oxide of zinc.

NON-METALLIC OR ACIDIC OXIDES.

Oxide of carbon (carbonic acid gas).

Oxide of chlorine (hypochlorous anhydride).*

Oxide of nitrogen (nitric anhydride).*

Oxide of phosphorus (phosphoric anhydride).*

Oxide of silicon (silica).

Oxide of sulphur (sulphurous anhydride).*

For the next inquiry use the same solutions of the oxides of potassium, phosphorus, and sulphur, but replace the magnesia by solution of lime, that oxide being more soluble in water. Take the solutions of potash and oxide of sulphur. Note the greasy feel of the one and the sulphurous smell of the other. Pour the one into a portion of the other, frequently stirring and testing the acidity or alkalinity by transferring a drop by means of a glass rod on to a piece of red or blue litmus paper, until the mixture is exactly *neutral* and has no action on either red or blue litmus. Note that the liquid has lost all greasy feeling and sulphurous smell. Evaporate it to dryness on a water bath, and note the crystalline residue or *salt*, a substance

^{*} So called because of their relation to the corresponding acids. Nitric anhydride is nitric acid without water.

which appears to be a compound of the two oxides employed, for it has lost the distinctive properties of each.

Repeat the operation with the solution of lime and oxide of phosphorus, pouring the latter into the former till a neutral mixture is obtained. The "salt" appears in this case to be a white insoluble compound of the two oxides. Filter and evaporate the filtrate to dryness. Should there be no residue, this must be the case.

The conclusions arrived at from these two instances are true for the oxides of other elements. They may be stated thus:—

Basic oxides are oxides of metallic elements; if dissolved by water they form alkaline liquids, and they unite with acidic oxides forming salts.

The oxides of non-metallic elements are usually acidic; if dissolved by water they form acids, and they unite with basic oxides to form salts.

Salts are compounds formed by the admixture of basic and acidic oxides; if dissolved by water they usually form neutral solutions.

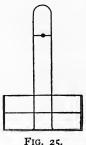
It will be observed that water is a neutral oxide. Thus basic and acidic oxides can be dissolved in water without their properties being affected. The element hydrogen, in fact, in its chemical behaviour, stands intermediate between metals and non-metals.

XIII. THE METALS: THE METALLIC OXIDES

In order to compare the chemical activity of the metals, a study may be made of their oxidisability and the methods by which their oxides may be produced. Two methods have already been found available for preparing oxide of iron from metallic iron, viz. (1) the action of the free oxygen of the air and (2)

the action of the combined oxygen of water, hydrogen being in this case liberated. These two methods may be tried in the case of other metals.

Cut small pieces of potassium and sodium the size of small peas. Note that on exposure to air, even when cold, the freshly cut surfaces become immediately tarnished, a film of oxide being formed. Throw the bits into a little pure cold water in a dish. Note that both metals quickly disappear, a gas being evolved. In the case of the potassium, but not in the case of the sodium, this gas catches fire spontaneously, showing that the heat produced by the chemical combination of potassium and oxygen is greater than that of sodium and oxygen, and that the chemical activity of the former, in respect to oxygen, is greater than the latter. Note that the flame is tinged violet, due to a little of the potassium being volatilised, this being the colour of the incandescent vapour of potassium and its compounds. Set fire to the gas being liberated by the sodium, and note that this is coloured yellow by the sodium vapour. To identify the gas, invert a test-tube of water in the dish (Fig. 25), and quickly insert small bits of sodium on the



point of a penknife, until a test-tube nearly full of the gas is Shake the gas with the water remaining in the testtube, transfer by upward displacement of air to a smaller dry test-tube, and ignite it. In its lightness, in its combustibility, and in its producing moisture on the sides of the tube, when burnt, has the gas the properties of hydrogen? Now test the water in the dish with red litmus paper. Has it become alkaline, thus showing that the metallic oxides, potash and soda, have been formed and are dissolved in the water? Does

Potassium + oxide of hydrogen = oxide of potassium + hydrogen?

The vapours of many metals and of their volatile compounds impart characteristic colours to non-luminous flames. Thus, among other metals:—

Sodium imparts a yellow colour.

Potassium ,, violet ,,

Calcium ,, red ,,

Strontium ,, crimson ,,

Barium ,, green ,,

These colours are best observed by heating a little of the compound on the end of a platinum wire in the Bunsen flame. As many compounds are not volatile, it is best to moisten the substance on the wire with hydrochloric acid, volatile salts being thus produced. As potassium compounds are very often impure with sodium compounds, it is best to examine the flame for potassium through a solution of indigo, the blue of which absorbs the yellow of the sodium. These coloured flames are useful for detecting and identifying the metals in minerals, mineral waters, etc. This is best done by examining the spectra by means of the prism of a spectroscope, in which advantage is taken of the different refrangibilities of different coloured rays of light in order to decompose the light emitted by each incandescent vapour into its component colours. By this means it is possible to identify the metals with certainty even in complex minerals.

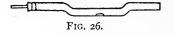
The metals calcium, strontium, and barium are so costly that their oxidisability cannot be practically investigated in this course. They assume a position, however, intermediate between the metals just studied and those next referred to.

Take pieces of magnesium ribbon and zinc foil. Note that in the air at ordinary temperatures the surface has very slowly become tarnished, but that the film of oxide gradually formed has preserved the metal beneath from further oxidation. Place each in a test-tube of water, and note that no gas is evolved, and therefore no oxide formed, even when the water is heated

to boiling (if the metals are pure). Ignite each metal in the Bunsen flame; note the similarity of the magnesia and the oxide of zinc formed. Test the alkalinity of the oxides by placing a little of each on a slip of red litmus paper and then moistening with water. Lastly, boil some water in a widenecked Florence flask, and plunge into the steam an ignited piece of one of the metals (preferably magnesium ribbon) held by the crucible tongs. Note that the metal burns brilliantly in the steam, the oxide being formed, while the escaping hydrogen catches fire and burns at the mouth of the flask.

Procure a piece of metallic iron. Note that, like magnesium and zinc, it is oxidised by damp air, but that, unlike those metals, the rust exfoliates and exposes a fresh metallic surface to further oxidation. (Iron vessels are, for this reason, often coated with tin which does not oxidise in damp air, or "galvanised" with zinc, the film of oxide forming on which does not exfoliate.) Note that the iron has no action on hot water. It has been already observed that iron heated to a low red heat decomposes steam. Note that the iron will not burn in the air, unless it be heated to a white heat by the oxyhydrogen flame, or unless it be in very small particles in the form of iron filings, these being more easily heated to the temperature of ignition, and presenting more surface for oxidation in proportion to their size.

Study the oxidisability of copper and mercury. Note that these do not oxidise in air in the cold. Heat some copper filings in an open crucible, and note that oxide of copper is



rapidly formed. Heat a little mercury in a tube (Fig. 26) through which a slow current of oxygen gas is passing, and note that the red oxide is formed on the tube just at the point at which condensation of mercury takes place, *i.e.*, just below

the boiling point. The chemical activity in respect to oxygen would seem to be greater in the case of copper, and this is also shown by the fact that while oxide of mercury is decomposed by heat, oxide of copper is not. In determining the composition of water, evidence has already been obtained that heated copper has no action on steam. In fact, under no conditions are these metals oxidised by water.

Study the oxidisability of gold, silver, and platinum. Note that under no conditions does direct oxidation take place (hence *noble* metals as distinguished from *base* metals). In fact, the oxides of these metals when formed by indirect methods are all decomposed on heating.

It is now possible to arrange the metals in the following groups:—

- 1. The metals of the alkalies (potash, soda, etc.), e.g. potassium, sodium.
- 2. The metals of the alkaline earths (lime, strontia, baryta), viz. calcium, strontium, barium.
- 3. The metals of the earths (magnesia, etc.), e.g. magnesium, zinc, iron.
- 4. The heavy metals, e.g. copper, mercury.
- 5. The noble metals, e.g. silver, gold, platinum.

This arrangement shows that the metals fall into natural groups, the members of each of which have several properties in common. Thus the metals that belong to the first group, because most oxidisable, form oxides both of which are characterised by their great solubility, while the metals which are classed in the second group, on account of their feebler oxidisability, all form oxides which are slightly soluble in water. In physical as well as in chemical properties this grouping often holds good. Thus sodium and potassium are found to be both characterised by low specific gravity and low melting point, and gold and silver are both characterised by

their great malleability and ductility and high conductivity for heat and electricity.

It is worthy of note that metals belonging to the same class are often associated with each other in nature. Thus gold and silver are invariably found together. Metals of weak chemical activity are usually found in the free state, e.g. gold, silver, and platinum, and occasionally copper and mercury. Metals of the other groups exist naturally in the combined state. Of such metals many occur as oxides. Loadstone and hæmatite, emery, tinstone, and pyrolusite are oxides of iron, aluminium, tin, and manganese respectively.

Physical Properties of the Metals.—Metals are distinguished from non-metals in their power of forming alloys with each other. This renders it possible to impart to a metal the colour, permanence, hardness, tenacity, etc., which is required. Thus brass—an alloy of copper and zinc which has the permanence of copper—is more useful because much harder. The following are the constituents of some of the principal alloys:—

British gold coin—gold, 22; copper 2 (22 "carat" gold, pure gold being

24 carat).

British silver coin-silver, 925; copper, 75.

British bronze coin-copper, 95; tin, 4; zinc, 1.

Brass-copper, 2; zinc, 1.

Aluminium gold-copper, 9; aluminium, 1.

Pewter-tin, 1; lead, 1.

Britannia metal—tin, 84; antimony, 10; copper, 4; bismuth, 2.

Type metal-lead, 75; antimony, 20; tin, 5.

Gun metal-copper, 9; tin, 1.

Common solder-tin, I; lead, 2.

An amalgam is an alloy with mercury.

The force of attraction that causes the cohesion of particles is exhibited to a different extent in different metals. When the cohesion is small, as in antimony and bismuth, the metals are brittle; when great, as in gold and silver, the metals are tenacious, malleable, or ductile. One grain of gold, the most malleable of all metals, can be beaten out into 56 square inches of gold leaf. One grain of silver, one of the most ductile of metals, can be drawn into 500 feet of wire. This cohesive force in metals is measured by the breaking strain.

Metals as a rule are good conductors of heat, but they differ in their conductivity. If upon one end of rods of several different metals a small piece of wax or phosphorus be placed, and the other end be heated, the heat will be conducted from one end to the other, as shown by the melting

of the wax or ignition of the phosphorus, in times varying with the metals employed. Siiver and copper are good conductors, bismuth and antimony bad conductors of heat. Good conductors of heat are also good conductors of electricity.

Metals expand when heated. In the construction of railways and iron bridges this fact has to be taken into account. Timepieces lose time in hot weather, owing to the expansion of balance wheels and pendulums. In chronometers advantage is taken of the different expansibilities of metals to provide for automatic regulation.

Metals differ in heat capacity. The heat capacity of mercury being very low (and its conductivity for heat being high), mercurial thermometers are sensitive to rapid changes of temperature.

Metals differ in their density. Sodium and potassium float upon water, but all the other common metals sink. All the commoner metals, with the exception of gold, float upon mercury, which is therefore one of the heaviest metals known.

Metals differ in their fusibility. Mercury is liquid at the ordinary temperatures; sodium and potassium both liquefy below the boiling point of water; tin and lead below a red heat; zinc and aluminium at a low red heat, and copper at a bright red heat; while iron only liquefies at a white heat. Alloying one metal with another often lowers its melting point; thus fine solder has a lower melting point than either the tin or lead of which it is an alloy.

Metals differ in their hardness. By comparing the power that solids have of scratching each other, their hardness can be roughly ascertained. Thus lead can be scratched by copper and copper by zinc. The presence of an impurity even in small quantities often alters the hardness. Thus steel, i.e. iron containing ½ to I per cent. of carbon, is much harder than iron. The hardness of steel also depends upon the rate of cooling. Thus steel which has been "tempered" by heating and slow cooling is much less hard and elastic than steel which has been cooled quickly.

The following table gives some of the physical constants for the principal metals:—

PHYSICAL PROPERTIES OF THE METALS.

	Specific Gravity.	Melting Point in Degrees Centigrade.	Specific Heat Capacity.	Relative Conductivity for Heat.	Relative Conductivity for Electricity.	Linear Expansion from o°C. to roo°C.	Breaking Strain in Pounds per sq. inch.
Iron .	7.8	1635	.112	991	103	71100.	50,000
Steel .	7.8	1360	811.	1111	52	60100.	150,000
Copper .	8.9	0111	.093	614	633	29100.	33,000
Zinc .	7.2	415	.093	303	178	.00298	7,500
Lead .	11.4	326	.030	84	52	.00271	1,900
Tin .	7.3	230	.056	153	92	.00230	4,700
Aluminium	2.7	625	.216	343	343	.00222	١
Gold .	19.3	1080	.032	1	478	.00147	١
Mercury .	13.6	- 39	.033	15	11	1	1

XIV. COMBINING WEIGHTS OF THE ELEMENTS

In the foregoing studies evidence has been accumulated that chemical combination takes place in definite proportions by weight, and that each element has its own combining weight. It was found that I part by weight of hydrogen, 3 parts by weight of carbon, and 100 parts by weight of mercury combine with 8 parts by weight of oxygen, forming respectively water, carbonic acid gas, and red oxide of mercury. The question must now be asked—Do these elements unite in these proportions only?

When lead is roasted in the air, the oxide of lead—litharge—is formed. On further roasting, at a gentle heat, the reddish yellow colour of the litharge darkens, and ultimately red lead is obtained. It has been already found that red lead at a higher temperature breaks up into litharge and oxygen. Red lead must therefore be an oxide of lead, containing a larger proportion of oxygen than litharge contains. Introduce about 5 grams of red lead, previously dried by heating on a water bath, into a weighed porcelain crucible, and weigh. Heat very gently, taking care not to melt the contents of the crucible, till oxygen ceases to be evolved, and the red lead is entirely reduced to yellow litharge. Allow to cool, and weigh. Calculate the proportions of litharge and oxygen per cent. of red lead.

Not only lead, but hydrogen, carbon, mercury, and, in fact, most of the elements, combine with oxygen in more than one proportion. The relation between the composition of the oxides, however, if there be more than one, is always a very simple relation. Thus in the two compounds of hydrogen and oxygen, the combining proportion in the one is 1 to 8, in the other 1 to 16. It is usual, therefore, to take as the combining weight of the element a simple number that represents the proportion in which it enters into its various combinations,

and to regard each compound as containing one, two, or more combining weights of the element.

If hydrogen, having the lowest combining weight, be taken as unity, that of oxygen is taken as 16, that of carbon as 12, and that of mercury as 200. Water would then contain two combining weights of hydrogen to one of oxygen, and may be represented as H₂O, taking H and O to represent respectively single combining weights of the elements. Carbonic acid gas would contain one combining weight of carbon to two of oxygen, and may be represented as CO₂, where C represents a combining weight of carbon. Red oxide of mercury would contain one combining weight of each element, and may be represented as HgO where Hg represents a combining weight of mercury (hydrargyrum).

In the earth's crust about seventy elements are known to exist, but of these it is only necessary to give the combining weights of twenty-two. These are:—

Aluminium (Al)	27	Mercury (Hydrargyrum,
Barium (Ba)	137	Hg) 200
Calcium (Ca)	40	Nitrogen (N) 14
Carbon (C)	I 2	Oxygen (O) 16
Chlorine (Cl)	35.5	Phosphorus (P) 31
Chromium (Cr)	52	Potassium (Kalium, K) 39
Copper (Cuprum, Cu).	63	Silicon (Si) 28
Hydrogen (H)	1	Sodium (Natrium, Na). 23
Iron (Ferrum, Fe) .	56	Strontium (Sr) 87
Lead (Plumbum, Pb) .	206	Sulphur (S) 32
Magnesium (Mg)	24	Zinc (Zn) 65
Manganese (Mn).	55	

THE composition of the compound which the element mercury forms with oxygen has been already determined. Of the other metallic elements in the foregoing list, it has been found by experiment that their most important oxides have the following percentage compositions:—

	Met	tallic	Oxide.				Metal.	Oxygen.
Alumina	•		•	•			52.9	47.1
Baryta .	•			•	•		89.5	10.5
Lime .							71.4	28.6
Oxide of chr	omiuı	m	•				68.4	31.6
Cuprous oxid							88.7	11.3
Cupric oxide	(the	blac	k oxid	e of c	oppe	r) .	79.7	20.3
Ferrous oxid	е				•	•	77.8	22.2
Ferric oxide	(the 1	ed o	xide o	f iron) .		70.0	30.0
Litharge .		•	•		•	•	92.8	7.2
Magnesia	•			•	•	•	60.0	40.0
Oxide of man	ngane	se		•			77.5	22.5
Peroxide of 1	manga	anese	the !	black	oxide	e) .	63.2	36.8
Red oxide of	merc	cury		•		•	92.6	7.4
Oxide of pot	assiur	n.	•	•	•		83.0	17.0
Oxide of sod	ium		•	•			74.2	25.8
Strontia .							84.5	15.5
Oxide of zine	с.						80.2	τ9.8

Calculate the number of combining weights of each element in the compounds, and express the results by the simplest possible formulæ. For example, if the quantities of magnesium and oxygen per cent. of magnesia be divided by their respective combining weights, viz. 24 and 16, the number of combining weights of the two elements will be found to be equal, viz. 2.5 for each element. Hence the simplest possible formula for magnesia is MgO. Having

obtained the formulæ, arrange the oxides in groups as monoxides, dioxides, and trioxides. Calculate the formula that most nearly expresses the composition of red lead as determined by the foregoing experiment.

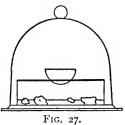
To distinguish the oxides of a metal, it is usual to specify the colour, or to use the terminations -ous and -ic to represent the lower and higher oxides respectively. Unstable higher oxides are usually distinguished as peroxides. The highest oxides of metals are sometimes acidic. There are, for instance, a chromium trioxide CrO₃, and manganese heptoxide, Mn₂O₇, which exist combined with potash in "bichromate of potash" and "permanganate of potash." The oxides of some metals, though basic, act as acidic oxides to more basic oxides. Thus alumina dissolves in caustic soda solution, forming a salt. This reaction serves to distinguish alumina from the other bases met with in agriculture.

It has already been observed that the basic oxides, if dissolved by water, form alkaline liquids, but they differ in their solubility. Of the oxides studied, potassium and sodium oxide will be found to be soluble in water in almost all proportions; lime, strontia, and baryta soluble to a limited extent; magnesia, litharge, ferrous oxide and oxide of zinc very slightly soluble; the remaining oxides practically insoluble. these statements experimentally. The act of solution appears to be accompanied by chemical combination, for heat is produced. Slake some quicklime with cold water. the change in appearance that takes place (immediately if the lime be pure, slowly if impure), the heating of the mixture, and the final disappearance of the water, all evidence of chemical combination having occurred. The compound produced (slaked lime) may be termed hydrate of lime.

Determine the proportions in which lime combines with water. Heat a weighed quantity—say I gram—of pure quicklime to low redness in a weighed capsule. Cover the capsule, allow to cool in a dessicator (Fig. 27) over more quicklime, itself a good drying agent, and, when cold, weigh, Add excess of water, cover with a beaker till slaking is complete, and place in the

dessicator for some hours. When dry, cover and weigh as quickly as possible. Replace in the dessicator for an hour,

and weigh again. Should the weight have changed, continue the dessication till the weight is constant. Having found the water combined with the lime, heat the capsule again to a low red heat to decompose the hydrate and drive off the water; cool as before, and weigh. Does the loss in weight tally with the previous gain in weight? If not, repeat the pro-



cesses until concordant results are obtained. Express the

result as percentage composition of slaked lime.

Most basic hydrates can be decomposed by heat, but not all. Caustic potash and caustic soda of commerce are the hydrates of potash and soda, and it is not possible to decompose these by heating to redness. Since the hydrates of basic oxides are compounds of metals with hydrogen and oxygen, they are frequently spoken of as metallic hydroxides; thus potassium hydroxide or hydroxide of potassium.

The approximate percentage composition of the more important hydrates of the metallic oxides is as follows:-

Basic Hydrate.	Metallic Oxide.	Water.
Hydrate of alumina (aluminium hydroxide) .	. 65.4	34.6
Hydrated oxide of copper (cupric hydroxide)	. 81.4	18.6
Hydrated oxide of iron (ferric hydroxide) .	. 74.8	25.2
Slaked lime (calcium hydroxide)	• 75-7	24.3
Caustic potash (potassium hydroxide)	. 83.9	16.1
Caustic soda (sodium hydroxide)	· 77·5	22.5

It is possible that if compounds unite, the proportions in which they combine will be the sum of the combining weights of the elements contained, or simple multiples thereof. Assuming that this be so, calculate the combining weights of water and the metallic oxides, and find the number of combining weights of each in each hydrate. Ascribe the simplest possible formulæ

to the compounds, regarding them both as hydrates of metallic oxides, e.g. MO.H₂O, and as metallic hydroxides, e.g. M(OH)₂, where M stands for any metal uniting with oxygen in single combining proportions. Arrange them in groups of mono-, di, and tri-hydroxides.

The result of these calculations will show that the assumption on which they were founded was perfectly justified. Indeed, it may now be surmised that, not only do elements in general unite in the proportion of their combining weights, or in simple multiples of them, but that the proportion in which a compound unites with another compound is the sum of the combining weights of its elements or a multiple thereof.

XVI. THE NON-METALLIC ELEMENTS: SULPHUR

It has been found that non-metallic elements are characterised by forming anhydrides, *i.e.* oxides which, when combined with water, form acids; whereas metals form basic oxides which combine with water, forming basic hydrates. The elements which are non-metallic in this sense are further characterised by absence of metallic lustre. In this respect oxygen must be classed as a non-metallic element; indeed, in that it forms compounds with hydrogen and the metals, it may be regarded as a typical non-metal. Just as the properties of oxygen and the oxides have been studied, so we have now to study the properties of the remaining non-metallic elements and their compounds with hydrogen and the metals, in addition to the compounds they form with oxygen, the acids formed by the union of the oxides with water, and the salts formed by union of acidic with basic oxides.

The non-metallic elements which have to be studied are sulphur, chlorine, nitrogen, phosphorus, silicon, and carbon. Of these, *sulphur* will first be considered.

Place some sulphur in a dry test-tube, and heat, using a test-tube holder. Note the melting of the sulphur and the singular changes in the colour and viscosity of the liquid, till the boiling point is reached. Note that the deep red vapour ignites spontaneously as it issues from the tube, this temperature being high enough to promote rapid chemical combination between the sulphur and the oxygen of the air, the sulphuroussmelling oxide being formed. Pour the remaining liquid in a thin stream into cold water, and note the plastic consistency of the rapidly cooled sulphur. Dissolve some ordinary sulphur in a little bisulphide of carbon, and allow the clear liquid to evaporate spontaneously in a dish. Preserve the octahedral crystals formed. Try to dissolve some of the plastic sulphur in the bisulphide of carbon, and evaporate the liquid. Note that no crystals are obtained, showing that plastic sulphur is insoluble. This is an instance of allotropy, that is, the existence of an element in "another condition" having different properties.

Does sulphur, being a non-metallic element like oxygen combine with metals and with hydrogen? Mix together single combining proportions of sulphur and iron filings (about 10 grams in all), place the mixture in a narrow test-tube, and heat just the bottom of the test-tube strongly. Note that presently the contents of the tube begin to glow, heat being obviously produced, thus showing that chemical combination is occurring, and sulphide of iron is being formed.

Sulphur is found in Sicily and other volcanic districts in the free state, but it occurs more abundantly in nature combined with metals. Thus galena, stibnite, cinnabar, iron pyrites, and zinc blende, are native sulphides of lead, antimony, mercury, iron, and zinc respectively. Copper pyrites is a double sulphide of iron and copper. With the exception of iron pyrites, all these ores are used as sources of the metals.

It has been noticed that there are metals which, when placed in dilute sulphuric acid, cause the evolution of hydrogen gas. It is possible that if the sulphides of these metals were placed in dilute acid, the sulphide of hydrogen would be produced. Try the sulphide of iron just obtained. Note that the escaping gas is distinguished from hydrogen by its foul smell. Ignite it. What are the two products of combustion, and what evidence do these yield that the gas is indeed the sulphide of hydrogen, or *sulphuretted hydrogen*? The percentage composition is found by analysis to be:—Sulphur=94.11%, hydrogen=5.88%. What is the simplest formula that would represent the compound?

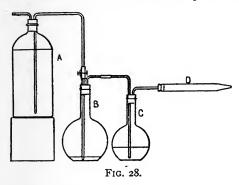
When organic matter containing sulphur decays, the sulphur is set free combined with hydrogen. This accounts for the smell of rotten eggs, the white of egg consisting of sulphur compounds. Rotting cabbages and turnips have a similar odour, these being also rich in sulphur compounds. The water of many springs is impregnated with sulphuretted hydrogen, notably the Harrogate waters.

The composition of sulphuretted hydrogen shows that, like oxygen, a single combining weight of sulphur combines with two of hydrogen. In other words, sulphur is able to *replace* oxygen, and this is true, not only of the compound with hydrogen, but also of compounds with other elements. Thus, the formula for ferrous oxide was found to be FeO; that for the ferrous sulphide just prepared is FeS.

Burn some sulphur in a jar of air or oxygen. Shake the gaseous sulphurous anhydride produced with water in order to form a solution of sulphurous acid. Preserve a portion of the solution in a corked test-tube, and expose the remainder in a shallow dish to the air, or allow air slowly to bubble through it. Note that after some time the smell of sulphurous acid disappears from the liquid in the open dish, yet it still remains acid to litmus, while in the closed tube the sulphurous acid is unchanged. The sulphurous acid has apparently become oxidised by the air to an acid which is odourless. What is the

anhydride of this new acid, and is it possible to obtain it by the oxidation of sulphurous anhydride?

To investigate these questions, fit up the apparatus figured. In the combustion tube D, near the drawn-out end, place some platinised asbestos, *i.e.* asbestos on which platinum has been deposited in a finely divided state. In C place a strong solution of sulphurous acid (supplied). Allow water to syphon from A to B in order to drive air through the solution of sulphurous acid, so that a mixture of air and sulphurous anhydride, evolved from the acid, will pass through D.



Now heat the platinised asbestos in D. Judging from the altered smell and appearance of the issuing vapours, is oxidation of the sulphurous anhydride now taking place? Allow the asbestos to cool, and heat an empty portion of the tube. Does oxidation now occur? Now heat the platinised asbestos again, and pass the vapours into water by means of a glass tube attached to D. Note whether an odourless acid solution is obtained similar to that formed by the slow action of the air on solution of sulphurous acid.

This experiment indicates that sulphurous anhydride and oxygen do not combine under ordinary conditions even when heated, but combine when brought into contact with hot

finely divided platinum, an instance of chemical action being brought about by contact with a third substance ("contact action"). On the other hand, sulphurous acid is directly oxidised at ordinary temperatures. The two anhydrides and acids may be distinguished as sulphurous and sulphuric. Analysis shows that equal weights of sulphur and oxygen are combined in sulphurous anhydride, and that sulphuric anhyd ide contains of oxygen half as much again. What formulæ should be ascribed to the two compounds?

The use of the fumes of burning sulphur, in presence of water vapour, as a bleaching agent, is partly due to the oxidation of sulphurous to sulphuric acid at the expense of the combined oxygen of the colouring matter, colourless substances being formed. In presence of water vapour the fumes are also a useful disinfectant, probably for the same reason.

XVII. SULPHURIC ACID

It is found by experiment that a single combining weight of water combines with a single combining weight of sulphuric anhydride to form sulphuric acid. Its formula is therefore $SO_3.H_2O$ or H_2SO_4 . The "oil of vitriol" of commerce is sulphuric acid, with 2 to 6 per cent. of additional water. Its specific gravity is 1.84.

Pour some oil of vitriol into a small beaker containing water. Is there any evidence of chemical combination and the formation of a hydrate of sulphuric acid? Expose some strong sulphuric acid in a beaker to the air for a few days. Does the liquid increase in volume, indicating absorption of water vapour? The chemical attraction between sulphuric acid and water may be made use of for drying gases.

In what proportion does sulphuric acid unite with bases to form salts. Pour some pure sulphuric acid of known strength into a small flask, cover with a watch glass, and weigh. Transfer

about 25 c.c. to a $\frac{1}{2}$ -liter flask containing some distilled water, and weigh the small flask again. Now add distilled water to the $\frac{1}{2}$ -liter flask till the liquid measures $\frac{1}{2}$ -liter at 15° C. Calculate the strength of the dilute acid, *i.e.* the weight of pure sulphuric acid in 1 c.c. of the liquid.

Into a small wide-mouthed flask quickly place several small dry lumps of caustic soda, cork the flask, and weigh. Quickly transfer I or 2 grams of the caustic soda to a

350 c.c. flask containing about 50 c.c. of distilled water, recork the weighing flask, and weigh again to find the exact weight of caustic soda taken. Weigh out a second quantity of caustic soda into a second flask containing water, and marked with a file to distinguish it from the first. Allow the caustic soda to dissolve in the water in each flask, and add a few drops of solution of litmus till the liquid is just rendered blue. Fill a burette with the diluted sulphuric acid till the top mark exactly coincides with the bottom of the meniscus of the liquid when viewed exactly on the level, the burette being perfectly upright. Allow the acid to run into the caustic soda, constantly

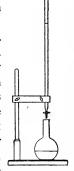


Fig. 29.

shaking the flask meanwhile, till the blue colour of the litmus is changed to purple. Boil the liquid and add a few more drops of acid till again perfectly neutral; repeat the process till a permanent purple colour is obtained. Having read off the amount of acid used, add one more drop of acid. If previously neutral, this will turn the liquid red. Treat the second solution of caustic soda in the same way. If the results be not concordant, a third and fourth determination must be carried out. Calculate the reacting proportion of sulphuric acid and caustic soda. Does it agree with that expressed by the formulæ—

 $Na_2O.H_2O + SO_3.H_2O$ or, $2NaOH + H_2SO_4$? In chemical formulæ and equations a small figure placed after a symbol is held to refer to that symbol only. A large figure placed in front of a symbol is held to govern the whole group of symbols. A point (.) between two groups of symbols indicates that they are combined together. A semicolon (;) is used to indicate a looser combination of compounds with each other. A plus sign (+) between two formulæ indicates that the substances are mixed together, while the sign = points to reaction having occurred between them and an equal weight of new substances formed.

In volumetric determinations it is very important that the measurements should be systematically entered in the notebook. The following will serve as an illustration:—

Weighing flask and caustic soda . Weighing flask		11. 20. 169 grams. 17.761 ,,	
Caustic soda taken Sulphuric acid used (1 c.c. = .098	2.240 ,,	2.408 ,,	
grams H ₂ SO ₄) and from this the quantity of sulphu combining weight of caustic soda show	ric acid combir	ning with a sing	le

Basic and acidic oxides combine to form salts. When caustic soda and sulphuric acid react, each being the hydrate of the respective oxides, in addition to *sulphate of soda*, water would also be produced, as expressed by the equation—

$$Na_2O.H_2O + SO_3.H_2O = Na_2O.SO_3 + 2H_2O$$

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

so that the resulting salt would weigh less than the sum of the reacting substances by two combining weights of water. To test the truth of this assumption, evaporate one of the neutral solutions to dryness in a weighed dish on the water bath, heat strongly for a few minutes over the bunsen flame, cool in the desiccator, and weigh the anhydrous salt.

XVIII. THE SULPHATES

The sulphates of other bases can be prepared like sulphate of soda by neutralising sulphuric acid with the basic oxide or its hydrate. Many of these sulphates occur in nature, or are of importance in commerce. Procure and examine the following:—

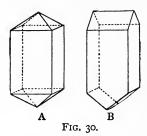
Note that these salts are crystalline. Expose a weighed crystal of sulphate of soda to the air; observe that it effloresces and loses its crystalline form and decreases in weight. Heat a crystal in a test-tube; note that it liquefies, water vapour escapes, and the salt finally dries up as a white amorphous (i.e. formless) mass. The crystalline salt is therefore a hydrate of sulphate of soda. Many other salts combine with water forming crystalline compounds. This water of crystallisation is generally loosely combined, sometimes escaping at the ordinary temperature in dry air, and usually at 100° C., but occasionally needing a much higher temperature for complete dehydration.

Determine the water of crystallisation of gypsum, or its crystalline form, selenite. Heat a weighed quantity (say .5 gram) of the finely powdered material in a weighed porcelain capsule in the water oven at a temperature of 100° C. until no further appreciable loss of weight occurs. (Before each weighing the capsule must be cooled in the dessicator.) Having obtained the exact weight, raise the temperature to a low red heat until the weight is again constant. The residue is anhydrous sulphate of lime. Calculate the percentage composition of the original gypsum,

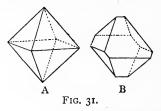
and of the intermediate hydrate, and represent them by formulæ.

The intermediate hydrate, which should have a composition represented by the formula 2CaSO₄. H₂O, is "Plaster of Paris." This, when mixed with a little water, combines and sets to a hard mass of gypsum. Plaster of Paris is prepared by heating gypsum. If the temperature be raised too high, the anhydrous sulphate, which combines with water very slowly, is formed, and it becomes useless as a plaster.

Observe that each of the six salts is distinguished by a different crystalline form. Examine the crystals of Epsom salt with a lens. Note that each crystal is a *prism*, having the form A (Fig. 30) or the modification B. Recrystallise some of the



alum by dissolving in hot water and allowing the solution to cool. Note that each crystal is an octahedron having the form A (Fig. 31), or, owing to undue development of opposite faces



of the crystal, the modification B. Select one of the most perfect crystals, suspend it by means of a hair from a glass rod,

then having filtered the solution of alum into a beaker, rest the rod across the top of the beaker as figured, so that the crystal

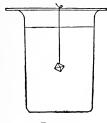


FIG. 32.

remains suspended in the solution. Watch the gradual growth of the octahedron. Observe that in the case of selenite (Fig.

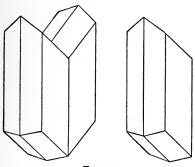


Fig. 33.

33) the crystals are connected together in the form of "twin crystals."

It has been noticed already that whereas zinc only when strongly heated attacks water with liberation of hydrogen and formation of oxide of zinc, it readily attacks water acidified with sulphuric acid, hydrogen being briskly evolved and a clear liquid left, in which, it is to be expected, the salt produced by the action of sulphuric acid on oxide of zinc is dissolved.

$$Zn + H_2O = ZnO + H_2$$
; but $Zn + H_2O.SO_3 = ZnO.SO_3 + H_2$

Dissolve zinc in dilute sulphuric acid, and, when action ceases, pour off the clear liquid from the excess of zinc and evaporate on a water bath until, on cooling, crystals are obtained. When quite cold, drain the crystals and purify them by recrystallisation, i.e. by redissolving in pure water and evaporating till crystals are again obtained. Dry by pressing between folds of filter paper and preserve. Note that the crystals are isomorphous (of the "same form") with those of Epsom salt, showing that even in respect to the properties of their compounds these metals belong to the same class.

Only metals which are able to attack water, such as sodium, calcium, zinc, and iron, are able to attack dilute sulphuric acid. Copper and mercury are without action on the dilute acid, but their sulphates can, of course, be obtained by the action of sulphuric acid on their oxides. Nearly all the common metals are oxidised when heated with strong sulphuric acid, sulphurous anhydride and water being produced; the oxides formed react with more of the sulphuric acid forming the corresponding sulphates. It should be noted that the compound that acts as an oxidising agent is itself reduced; the substance that acts as a reducing agent is itself oxidised.

While the formula equation given above represents the chemical change in a simple way, it must not be supposed that the arrangement of the elements in the compounds is in any way represented. The change in fact might be represented more correctly thus:—

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

in which the group SO_4 is regarded as combined with hydrogen in the acid and zinc in the salt, the acid being sulphate of hydrogen and the salt sulphate of zinc. There are many reasons for preferring this nomenclature for metallic salts. To take the simplest reason, it is inconvenient to speak of sulphate of oxide of zinc, sulphate of oxide of iron, and sulphate of oxide of copper. It is usual to call these substances—

Sulphate of zinc (white vitriol) ZnSO₄·7H₂O
Sulphate of iron (green vitriol) . . . FeSO₄·7H₂O
Sulphate of copper (blue vitriol) . . . CuSO₄·5H₂O
and, to be consistent, to speak of the sulphates of sodium, potassium, mag-

nesium, calcium, etc., instead of the sulphates of soda, potash, magnesia, lime, etc. The latter terms are, however, always employed in agriculture, and it is very important that the student should be familiar with them and understand their meaning.

When the solution of a free base or acid is added to the solution of a salt of a different base or acid, reaction occurs. Thus, if solution of caustic potash be added to a solution of sulphate of sodium, sulphate of potassium is formed and caustic soda set free, to an extent depending upon the amount of caustic potash added, till an equilibrium is established between the substances. But when the combined base or acid is volatile and therefore escapes from the liquid, or is insoluble and therefore is precipitated, more of the free base or acid will take its place, until, if sufficient of the free base or acid has been used, complete change has occurred. To a solution of sulphite of sodium, i.e. the salt produced by the action of sulphurous acid and caustic soda on each other, add strong sulphuric acid. Note that sulphurous acid is set free as indicated by its smell, and being unstable, decomposes, gaseous sulphurous anhydride being given off. To solution of sulphate of copper add solution of caustic soda till the mixture is alkaline in reaction. Note that the blue hydroxide of copper is precipitated, and that this, when the mixture is heated, loses water and is converted into the familiar black oxide. Filter the mixture and evaporate the now colourless filtrate; crystals of sulphate of sodium should be obtained. Write equations to represent the changes. These facts are of great importance because they provide methods for preparing acids and bases which cannot be directly or conveniently prepared from the elements.

Insolubility or volatility conditions, not only the formation of a base or an acid, but also the formation of a salt. The sulphate of barium is insoluble in water. If, then, to a solution of sulphuric acid or a sulphate, a solution of baryta or a soluble barium salt be added, sulphate of barium will be precipitated. As this is the only insoluble barium salt unattacked by, and

therefore insoluble in, acids, the reaction provides a test for sulphuric acid and the sulphates. To (1) distilled water, (2) tap water, and (3) solution of sodium sulphate, add a few drops of baryta water and then nitric acid. A permanent white precipitate will be obtained where sulphate was present. Write an equation representing the reaction between sodium sulphate and baryta.

XIX. COMMON SALT: HYDROCHLORIC ACID

OF the salts examined, so far none correspond in taste and appearance with common salt. Recrystallise some common salt by evaporating an aqueous solution till crystallisation

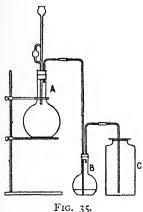


begins; then allow to stand. Note that each crystal has the form of a cube (Fig. 34). When carefully crystallised, the cubes build themselves together into hollow inverted pyramids. Insert a grain of salt on a platinum wire into a non-luminous flame; note the yellow coloration of the flame. What metal does this show

is present? Place some salt in a test-tube and add strong sulphuric acid. Is a volatile acid thus liberated? Test the vapour with blue litmus paper.

Prepare some of the acid from common salt in the apparatus In the flask A place 50 grams of salt, and in B just enough water to cover the bottom of the flask and the orifice of the glass tube, and thus to wash the gas as it passes through. Pour a little strong sulphuric acid through the funnel into A, adding more as required from time to time to produce a constant flow of gas. Heat gently when necessary. When the water in B has become saturated, collect the gas by

downward displacement in C. Does the gas burn or support the combustion of a taper? Remove the delivery tube, cover



the orifice with a glass plate, insert in a trough of water, and at the same instant remove the plate. Is the gas soluble in water? Now cause the gas to bubble into water till a saturated solution is obtained. Is the solution acid to litmus and sour in taste? Neutralise a little with caustic soda, and evaporate. Are cubic crystals obtained having the taste of common salt?

By the early chemists all acids were supposed to be oxygen compounds, and the acid from salt was called muriatic acid, salt being supposed to be muriate of soda. The acid might, however, be the hydrogen compound of a non-metallic element, just as sulphuretted hydrogen, the solution of which is also acid to litmus, is the hydrogen compound of sulphur. In this case, common salt would be the compound of this non-metallic element with sodium. This is now known to be the case; the non-metallic element is chlorine, the acid is hydrogen chloride or hydrochloric acid, and "salt" is chloride of sodium. Hydrochloric acid and sodium chloride have been found by experiment to contain 97.25 and 60.6 per cent. of chlorine respectively. What are the simplest formulæ that represent their composition?

What are the reacting proportions of caustic soda and hydrochloric acid? If chloride of sodium be obtained by neutralising hydroxide of sodium with chloride of hydrogen, hydroxide of hydrogen (water) must be set free, and the salt will weigh less than the base and acid taken by the water formed. Investigate these problems by the following experiment.

First find the strength of the saturated solution of hydrochloric acid prepared in the preceding experiment. This can be done most easily by determining the density, as the density of a liquid varies with the dissolved constituents. Make two determinations at 15° C. by the U tube method (Fig. 18), and calculate the strength from the following figures:—

Relative Densities of Solutions of Hydrochloric Acid at 15° C.

Relative Density.	Percentage by Weight.	Relative Density.	Percentage by Weight.	Relative Density.	Percentage by Weight.
1.100	20.06	1.135	27.04	1.170	34.02
1.105	21.06	1.140	28.04	1.175	35.01
1.110	22.06	1.145	29.03	1.180	36.01
1.115	23.05	1.150	30.03	1.185	37.01
1.120	24.05	1.155	31.03	1.190	38.01
1.125	25.05	1.160	32.02	1.195	39.00
1.130	26.04	1.165	33.02	1.200	40.00

Weigh out 25 grams of the acid into a quarter-liter flask, and make up to 250 c.c. with distilled water measured at 15° C. Fill a burette with the dilute acid. Weigh out two portions of caustic soda (say 2 grams each) into two flasks, dissolve in water, add enough litmus solution to render just blue and titrate with the acid, using all the precautions described in Study XVIII. When concordant results have been obtained, calculate the reacting proportions of caustic soda and hydrochloric acid. Do they correspond with the equation

given below? Now transfer the neutral liquids to weighed porcelain dishes, evaporate on the water bath to dryness, and weigh. Is the weight of salt obtained less than the weight of caustic soda and hydrochloric acid used by the weight of water that would be set free according to the equation—

$NaOH + HCl = NaCl + H_2O$?

The existence of acids, which are compounds of non-metallic elements with hydrogen, as well as those which are compounds of acidic oxides with water, and which may be distinguished as oxy-acids, makes it necessary to extend the meaning of the term "acid" to compounds containing hydrogen that is replaceable by metals with the formation of salts. The term salt, too, must not be restricted to compounds of basic and acidic oxides, but includes compounds which, formed by the action of bases on acids with liberation of water, are compounds of metals and non-metals.

Metallic chlorides occur very abundantly in nature. Enormous deposits of rock-salt, i.e. chloride of sodium, usually mixed with a little chloride of magnesium, which renders it deliquescent, and sulphate of calcium, are found in many parts of the world. In England the principal deposits are in Cheshire, where the salt is obtained by mining or by evaporating the brine pumped from shafts sunk into the salt. In the North Sea the water contains about 2.7 per cent. of sodium chloride and 0.5 per cent. of other chlorides and sulphates, while in the Atlantic Ocean the water contains about 3.3 per cent. of sodium chloride, and 0.3 per cent. of the other salts. At Stassfurt, in Germany, there exist large deposits of "carnallite," KCl. MgCl2; 6H2O, from which the so-called "muriate of potash" (chloride of potassium), used as an artificial manure, can be obtained by simply dissolving the salt in water and evaporating till crystallisation commences, the magnesium chloride and part of the potassium chloride being left in solution. In the same deposits the "kainite," K₂SO₄. MgSO₄. MgCl₂; 6H₂O, is found, which is also so largely used as a manure. Small quantities of bromides and iodides, the corresponding salts of bromine and iodine, two elements of properties analogous to chlorine, are frequently found associated with chlorides.

The chloride of silver is an insoluble salt of characteristic appearance. Unlike other insoluble silver salts, it is not acted upon by acids, but combines with ammonia, forming a soluble compound. The solution of a chloride may therefore be distinguished by its giving a white precipitate with a solution of nitrate of silver, insoluble in nitric acid, but soluble in solution of ammonia. Test (1) distilled water, (2) tap water, and (3) brine, for chlorides.

XX. CHLORINE

How can the element chlorine be obtained? If it were possible to oxidise the hydrogen of hydrochloric acid to water by means of the oxygen of the air, or an oxide which easily loses a portion of its oxygen, such as red lead, chlorine might be set free. Compare the action of litharge and red lead on hot concentrated hydrochloric acid. Note that in each case a salt—the chloride of lead—crystallises out when the liquid cools, but that with red lead a new gas of characteristic odour is given off. The reactions, though they no doubt take place simultaneously, may be expressed in three stages as follows:—

Red lead = litharge + oxygen. Litharge + hydrochloric acid = chloride of lead + water. Oxygen + hydrochloric acid = chlorine + water.

Express these equations by chemical formulæ. The composition of chloride of lead has not yet been referred to, but if lead combines with oxygen, oxygen with hydrogen, and hydrogen with chlorine in the proportions represented by the formulæ PbO, OH₂, and HCl (Fig. 36), the probable formula can be deduced.

For the preparation of chlorine gas, the peroxide of manganese is more economical than red lead. Place about 50

ganese is more economical than red lead. grams in the flask A (Fig. 35), pour in some commercial hydrochloric acid (the impurities, viz. ferric chloride and sulphuric acid, cannot interfere with the reaction), mix thoroughly, and warm very gently. Pass the escaping gas through water in B, and collect some bottles of chlorine gas by downward displacement of air. Then pass the gas into



Fig. 36.

a flask of cold water and prepare a saturated solution of chlorine. The experiment must be conducted in a fume chamber, as chlorine gas is highly injurious to inhale.

Note the colour and smell of chlorine. Insert a jet of burning hydrogen into one of the bottles. Note that the gas is incapable of being set fire to in the air, but that it supports the combustion of hydrogen with production of white fumes. Is hydrochloric acid the product of combustion? Let the fumes dissolve in a little water shaken in the bottle, blow air through the solution till free from chlorine, and test for the acid

with blue litmus paper, and also with silver nitrate solution. In another bottle of the gas place a glowing splint. Is chlorine able to support the combustion of ignited carbon? Now thrust a lighted taper into the gas. Note the formation of the fumes of hydrochloric acid and the liberation of carbon, the paraffin wax of the taper being a compound of hydrogen and carbon. Ignite some metallic sodium in an iron deflagrating spoon, and place in another jar of the gas. What is the product of combustion? As a result of these experiments state whether chlorine is able to unite directly with oxygen, hydrogen, carbon, or sodium.

Fill a long glass tube, closed at one end, with the saturated chlorine water, and invert it into a small widenecked flask also filled with the chlorine water. Slip a

Fig.

37.

cork down the tube so as to fit loosely into the flask and prevent loss of chlorine. Invert the whole apparatus for a moment to get rid of any air which has got into the tube. Set the apparatus in bright sunlight for a few hours. Note that two or three inches of gas collect in the tube and that the liquid becomes colourless. When the gas ceases to be evolved, test it with a glowing splint. Is it oxygen? Has the hydrogen of the water been attacked by the chlorine forming hydrochloric acid and liberating oxygen, thus:—

$$Cl_2 + H_2O = 2HCl + O$$
?

Test the liquid for hydrochloric acid with silver nitrate solution, and with blue litmus paper.

Bleaching Agents and Disinfectants.—The strong attraction that the foregoing experiment shows to exist between chlorine and hydrogen causes chlorine to be a powerful oxidising agent, and upon this depends its use for bleaching, and as a disinfectant and deodoriser. A piece of turkey-red cloth, when placed in a jar of chlorine, is bleached if moisture be present, the red dye being oxidised to colourless substance by the oxygen set free from the water by the action of chlorine upon it. Chlorinated lime, which may be produced on a small scale by passing chlorine gas through a glass tube containing a layer of slaked lime, and which consists of a compound of calcium chloride and calcium hypochlorite (the salt derived from the hypochlorous anhydride mentioned on p. 52), is more conveniently used. On the addition of dilute acid to the powder chlorine is rapidly evolved, and even the carbonic acid gas of the air very slowly liberates chlorine, so that it is sufficient to sprinkle the powder wherever it may be required as a disinfectant or deodoriser. Another powerful oxidising agent and disinfectant is the permanganate of potash, K2O. Mn2O2, contained in Condy's Fluid, for the heptoxide of manganese easily gives up oxygen, and is reduced to a lower oxide. Ozone, a condensed form of oxygen occurring in sea and country air, and the peroxide of hydrogen, are also powerful oxidising and, therefore, bleaching and disinfecting agents. It must be remembered that sulphurous acid owes its bleaching power partly to its reducing action, and therefore acts in the opposite way to the substances now under consideration.

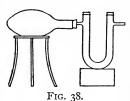
XXI. NITROGEN: AMMONIA

Previous experiments have shown that the gaseous element nitrogen is neither combustible nor a supporter of combustion. The German and French names for nitrogen—stickstoff and azote—express its inability to support life when respired. It was found that atmospheric air consists mainly of a mixture of oxygen and nitrogen in the proportion of about 1 to 4, or more exactly 20.9 and 79.1 per cent. by volume. This atmospheric nitrogen contains, however, about 1 per cent. of argon, a gaseous element of still greater inactivity.

In the combined state, nitrogen is an essential constituent of all animal and vegetable organisms. When nitrogenous organic matter decays, or when it is destructively distilled, the hydrogen compound of nitrogen, ammonia, is produced, just as sulphuretted hydrogen is produced from organic matter containing sulphur. Heat some horn shavings in a test-tube. Note the pungent smell of the escaping ammonia gas ("spirit of hartshorn"). Test the gas with litmus paper. Has it an acid reaction like the hydrogen compounds of sulphur and chlorine, or has it an alkaline reaction? If the latter, it is a base, and able to unite with acids forming salts. Hold a glass rod moistened with hydrochloric acid to the mouth of the tube. Is there any evidence of a salt, the hydrochloride of ammonia, being formed? Analysis shows that ammonia contains 82.35 per cent. of nitrogen and 17.65 per cent. of hydrogen. What is the simplest formula that would represent its composition?

Procure some commercial sal-ammoniac, the hydrochloride of ammonia. Note its fibrous crystalline structure, its solubility in water, its neutrality to litmus. Ammonia being a volatile base, it may be prepared from this salt by taking advantage of the facts stated on p. 77. Mix a little salammoniac with any fixed base, e.g. lime, potash, soda, etc.

Is ammonia set free? Fit up the apparatus figured. Fill the U tube with small lumps of quicklime to serve as a drying



agent. In the Florence flask place a mixture of 20 grams of powdered sal-ammoniac with twice its weight of powdered quicklime, then fill up the flask with lumps of quicklime, and, having connected the U tube, warm gently. Collect the gas in an inverted jar by upward displacement

of air. Note the colour, smell, and lightness of the pure ammonia. Of its two component gases, neither are supporters of combustion, and hydrogen alone is combustible. Examine the properties of ammonia in these respects. Pass a rapid stream of the gas into a flask containing a little cold water. Is it soluble? Prepare a saturated solution. Neutralise a little of the solution with hydrochloric acid, and evaporate to dryness. Is sal-ammoniac left?

With respect to the combustibility of ammonia, it must be remembered that while heat will be produced by the combustion of the hydrogen, heat must first be absorbed in order to decompose the ammonia into its elements. Hence, while there is a tendency for the gas to burn while the lighted taper is held at the mouth of the jar, the combustion immediately ceases when the heat of the burning taper is removed.

Determine the relative density of ammonia gas by means of the density flask (Fig. 1). To do so recharge the ammonia apparatus and attach a second U tube filled with quicklime to dry the gas thoroughly. Pass a slow stream of the ammonia into the top of the density flask until the gas issuing from the long tube is completely soluble in water. Compare the density (1) with air as unity, and (2) with hydrogen as unity.

Ammonia differs from the bases so far considered in not being an oxide. Its action on acids to form salts must therefore be different from that of caustic potash or caustic soda. It may be supposed that ammonia would unite directly with acids thus:—

$$NH_3 + HCl = NH_3 \cdot HCl$$

 $2NH_3 + H_2SO_4 = (NH_3)_2 \cdot H_2SO_4 \cdot$

To test the truth of this conjecture, place 20 cubic centimeters of the diluted sulphuric acid of known strength, prepared for Study XVIII., in a weighed dish, add the solution of ammonia, prepared above, in slight excess (the excess will volatilise), evaporate the solution to dryness on the water bath, and weigh. Does the weight of the compound obtained correspond with that calculated from the second of the formulæ given? Having found the formulæ for sal-ammoniac and the sulphate, write equations representing the action of quicklime upon them. Deduce the formula for calcium chloride from the formulæ of calcium oxide and hydrochloric acid.

Instead of the formulæ NH₃.HCl and (NH₃)₂.H₂SO₄, the compounds might be represented as NH₄Cl and (NH₄)₂SO₄, in which NH₄ is regarded as taking the place of hydrogen in the acids and a metal in the salts. The name *ammonium* is applied to this hypothetical metallic radicle, and the salts are called chloride of ammonium and sulphate of ammonium, like chloride of sodium and sulphate of sodium. In the same way the hydrate of ammonia, produced by dissolving ammonia in water, may be regarded as hydroxide of ammonium. Thus NH₄Cl, like NaCl, instead of NH₃.HCl; (NH₄)₂SO₄, like Na₂SO₄, instead of (NH₃)₂.H₂SO₄; NH₄OH, like NaOH, instead of NH₃.H₂O. The use in commerce of the term nuriate and sulphate of ammonia for chloride and sulphate of ammonium is obviously not justifiable.

Ammonium compounds are easily recognised, for they decompose when warmed with potash or soda, ammonia gas being set free. The gas can be distinguished by its smell, by its action on red litmus paper, and by the white fumes of sal-ammoniac produced when the mouth of the tube in which the test is made is brought near the mouth (or stopper) of the hydrochloric acid bottle. By this means, test a sample of "nitrogenous guano" and a sample of "barley manure" for ammonium salts.

XXII. NITRIC ACID AND THE NITRATES

NITROGEN, as its name implies, is a constituent of nitre or saltpetre. Insert a grain of this salt on a platinum wire into a non-luminous flame. What base does the coloration of the flame show that the salt is a compound of? Repeat the experiment with "Chili saltpetre." In what respect do the salts differ? Warm a little of each salt in test-tubes with strong sulphuric acid. Do the fumes of the acid evolved appear to be identical? Are they acid to litmus? Note that the vapour causes the inflammation of a glowing splint, showing that the acid is an oxygenated acid that readily loses oxygen?

These experiments show that saltpetre and Chili saltpetre are, respectively, the potassium and sodium salts of an *oxy-acid* (so called to distinguish acids which are the hydrates of acidic oxides from acids which are compounds of non-metallic elements with hydrogen). Being obtained from nitre, the acid is called *nitric acid*. It is the hydrate of nitric anhydride, N_9O_5 .

 $N_9O_5 + H_9O = 2HNO_9$.

A solution containing one gram of potash (K₂O) when exactly neutralised with a solution of nitric acid, and evaporated to dryness on a water bath, leaves a residue of nitrate of potassium weighing 2.149 grams. What formula will represent the composition of the salt? Judging from analogy, sodium and potassium having been found to resemble each other in all their chemical properties, what will be the formula for nitrate of sodium.

Prepare some nitric acid. Place about 25 grams of saltpetre in a retort (Fig. 14), and, by means of a thistle funnel thrust down the neck, add to it about 15 c.c. of strong sulphuric acid. Heat the mixture gently, using a rose burner, and collect the distillate in a flask kept cool by water.

Nitrogen is an element with apparently a weak attraction

for oxygen, for it is incapable of combustion in air or oxygen excepting at enormously high temperatures. It is to be expected, therefore, that nitric acid and the nitrates would lose oxygen easily and act as powerful oxidising agents. Pour a little of the strong nitric acid on to some red-hot charcoal contained in a crucible. Is there evidence of oxidation of the carbon? Mix together some powdered charcoal, sulphur, and nitre. Ignite the mixture. Do the charcoal and sulphur now burn so readily as to lead to the belief that the nitre provides the oxygen for combustion?

To act as an explosive, the combustible mixture must contain enough oxygen for combustion in absence of air. Its power as an explosive will chiefly depend upon the rapidity with which complete ignition occurs, and the amount of the gaseous products. The average composition of the gunpowders made at Waltham Abbey is:—Nitre, 74.5 per cent.; sulphur, 10.1 per cent.; charcoal, 14.1 per cent. The gaseous products of explosion, chiefly consisting of nitrogen and carbonic acid gas, occupy about 280 times the volume of these powders.

The oxidising effect of nitric acid renders its action on metals entirely different from that of dilute sulphuric acid. To a piece of granulated zinc in a test-tube add a little of the nitric acid. Note that the gas evolved is not hydrogen, it being incombustible. Repeat the experiment with granulated tin, and note that the tin is oxidised to the white oxide of tin. This can only be at the expense of the nitric acid, and the gases evolved must therefore be products of its reduction, either nitrogen itself, or gaseous oxides containing less oxygen than nitric anhydride.

These gaseous reduction products are:-

Nitrogen peroxide, NO2; a red gas.

Nitric oxide, NO; a colourless gas, but combining with oxygen to form the red peroxide.

Nitrous oxide, N₂O; a colourless gas, and powerful supporter of combustion like oxygen; does not combine with free oxygen. It is twenty times as soluble as oxygen.

Nitrogen, N; a colourless gas and non-supporter of combustion.

Probably all these gases will be present, but when the nitric acid is strong the higher oxides will predominate; when weak the lower oxides and nitrogen will predominate. The action of nitric acid on most metals results in the formation of a nitrate of the metal. Thus if copper be dissolved in nitric acid the nitric acid is reduced, and the oxide of copper formed dissolves in more of the nitric acid, forming a blue solution of copper nitrate. From this solution crystals of the salt may be obtained by evaporation. The reason why no nitrate is formed in the case of tin is that the higher oxide of tin is produced, and this, like some other higher metallic oxides, is an acidic, not a basic, oxide (see p. 64). It will have been noticed that in the preparation of nitric acid reddish coloured fumes of nitrogen peroxide were formed. This is due to the dissociation of the vapour of nitric acid by heat into nitrogen peroxide, water, and oxygen. Light has also the same effect, and a bottle of nitric acid exposed to sunlight soon becomes reddish in colour.

If during the action of the zinc on the nitric acid the liquid be kept very cold, it will soon acquire a green colour. The colour is due to the presence of *nitrous acid*, a very unstable compound soon decomposing into oxides of nitrogen and water. This acid combines with ammonia, forming nitrite of ammonium, but the salt is very unstable, for it decomposes even at the ordinary temperature into nitrogen and water as follows:—

 $NH_4NO_2 = N_2 + 2H_2O$.

This reaction provides a simple method for preparing nitrogen gas. Dissolve in water 25 grams of the nitrite of sodium, and place the solution in a flask connected with two wash-bottles, the first containing caustic soda solution, the second oil of vitriol. To the contents of the flask add ammonium chloride in the proportion represented by the formulæ NaNO₂+NH₄Cl, and warm gently. The mixture of salts will behave like nitrite of ammonium, and nitrogen will be evolved. Note that, when once the temperature is reached at which reaction commences, no further heat is required. Try to explain this. Pass the nitrogen into the density flask, and determine the relative density by the method described on p. 39.

Many other substances act as reducing agents on nitric acid.

Among these is ferrous sulphate, which is oxidised by this means to ferric salt. In this case nitric oxide is the product of reduction, and as this combines with the excess of ferrous sulphate to form a black compound, the reaction serves as a test for nitric acid and the nitrates.* To a very weak solution of saltpetre in a test-tube add a crystal of ferrous sulphate and allow to dissolve. Then very carefully, down the side of the tube, pour a few drops of pure strong sulphuric acid, so that it forms a layer at the bottom of the liquid. Note that a black ring is formed.

Another substance that reduces, and is oxidised by, nitric acid is indigo. To the very weak solution of saltpetre (a solution of I in 10,000 is quite strong enough) add an equal volume of pure, strong sulphuric acid, and, while the liquid is still hot, add a solution of indigo in sulphuric acid drop by drop. Note that the indigo is decolorised. The amount of indigo that can be decolorised serves as a rough comparative test for the quantity of nitrate present in two solutions. Test some distilled water, tap water, and the drainage water from arable land for nitrates by both methods.

All nitrates are soluble in water, so that there is no precipitant that serves as a test for nitric acid and the nitrates.

Putrefaction and Nitrification.—Saltpetre or nitre, the nitrate of potassium, is found as an efflorescence on the soil round villages in hot countries, due to the putrefaction of nitrogenous organic matter, the nitrification of the ammonia thus produced, and the combination of the nitric acid formed with the potash of the soil. By washing the soil with water the nitre is dissolved out, and may be obtained by evaporating the solution. The same series of changes may occur in a stable, where a strong smell of ammonia, due to the putrefaction of the manure, is sometimes observed, and crystals of nitrate of calcium found adhering to the mortar of the walls. In cultivated soil, too, these changes are constantly going on, especially in

 ^{\$\ \{2\}text{HNO}_3 = \text{H}_2\text{O} + 2\text{NO} + 3\text{O} \\
6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 + 3\text{O} = 3\text{Fe}_23\text{SO}_4 + 3\text{H}_2\text{O} \\
\text{FeSO}_4 + \text{NO} = \text{FeSO}_4\text{NO}\$

warm weather, and thus crops are provided with combined nitrogen in the form that plants most easily assimilate. The nitrate of soda (Chili saltpetre) occurring as a deposit in the rainless districts of South America, and which is now so largely employed (together with sulphate of ammonia) as a nitrogenous manure, owes its origin, no doubt, to the same cause.

Another very important application of these processes is the natural purification of water. When water has become contaminated with sewage, the nitrogenous organic matter serves as a food for disease germs which, under favourable conditions, multiply with enormous rapidity. But putrefaction of the organic matter and the nitrification of the ammonia produced deprives such germs of the means of development. In the analysis of drinking waters determinations are made of (1) the amount of total organic matter (as indicated by the quantity of permanganate of potassium it reduces. and therefore decolorises in presence of acid—see p. 84) expressed as "oxygen absorbed"; (2) the amount of nitrogenous organic matter expressed as "albuminoid ammonia"; (3) the amount of "free ammonia"; (4) the amount of "nitrates"; and (5) the amount of chlorides expressed as "chlorine." Should the albuminoid ammonia be high, recent sewage contamination is indicated, and the water would be condemned for drinking purposes. Should the free ammonia be high, the water would also be regarded with suspicion; but should the albuminoid and free ammonia be low, and the nitrates high, it indicates that sewage contamination has at some time occurred, but that sufficient time has passed for putrefaction and nitrification to go on, so that the water need not necessarily be condemned. The presence of much chlorine is suspicious, because common salt is an essential element of animal food, and therefore occurs in sewage, but the salt may be derived from other sources. The oxygen absorbed will be high if the organic matter be high, hence potassium permanganate provides a rough test for the purity of water from organic contamination. (Organic matter, however, is not necessarily highly nitrogenous.) Acidify a cylinder full of the water with a few drops of pure sulphuric acid, and then add a weak solution of permanganate, a drop at a time, until it is no longer decolorised after standing. Compare distilled water with tap water and rain water. Chlorides may be tested for with nitric acid and nitrate of silver, and nitrates with sulphuric acid and indigo solution.

The putrefaction of organic matter and the nitrification of ammonia are fermentative changes due to the action of micro-organisms. Among the conditions favourable to both kinds of fermentation are sufficient moisture, sufficient air, and sufficient warmth. That air must be necessary to nitrification is obvious when it is remembered that the conversion of ammonia into nitric acid is a process of oxidation, and since nitrate is the form of

combined nitrogen most easily absorbed by the roots of plants, the importance of cultivating the soil and admitting air is understood. One of the chief advantages of a long summer's fallow, in fact, is that nitrification can go on during a long period, and a large amount of nitrate formed for the ensuing crop. Since warmth favours fermentation, these changes take place principally in the summer months, so that crops growing in the summer and autumn are, other things being equal, more independent of an artificial supply of combined nitrogen than a crop growing in the spring. A fourth condition favourable to nitrification is a sufficiency in the soil of a base able to neutralise the nitric acid produced, for this acid, being a powerful oxidising agent, would otherwise destroy the nitrifying germs and therefore stop further nitrification. The base usually applied for this purpose, if there is insufficient in the soil, is lime.

The nitrates being all soluble in water, their loss by drainage is very great. At Rothamsted it was found that drainage water from uncultivated land contained on the average (19 years) as much as 5 grains per gallon of nitrates calculated as nitrate of sodium, a loss which amounted to 214 lb. per acre per annum. For this reason a long summer fallow should never be carried out on light soils through which water can easily pass, as the nitrate produced would thus be lost. It is moreover desirable, as far as is possible, that crops should always be growing on such land so as to utilise the nitrate as soon as formed. Salts of ammonia are not found to an appreciable extent in drainage waters, owing to their reaction with the double silicates of alumina and lime, magnesia or soda of the soil, the ammonia being fixed and a salt of lime, magnesia or soda, set free (see p. 99). For this reason sulphate of ammonia is sometimes preferred as a nitrogenous manure to nitrate of soda. It must, however, be remembered that since the ammonia has first to be nitrified, it is slower in its action on crops, and that owing to the formation of these insoluble compounds with soil constituents, it chiefly acts, when applied as a top dressing, on shallow-rooted plants.

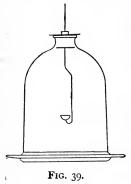
XXIII. PHOSPHORUS AND PHOSPHORIC ACID

THE element phosphorus, like nitrogen, is an essential constituent of all animal and vegetable organisms. When organic matter containing much phosphorus decays, the hydride of

phosphorus or phosphoretted hydrogen is often liberated. It is a gas of an odour even more offensive than sulphuretted hydrogen, and to it the smell of rotting fish is partly due. Iron is often impure with phosphide of iron. Such iron, when treated with dilute sulphuric acid, yields hydrogen mixed with phosphoretted hydrogen (compare with sulphur, p. 68), and this may be detected in the smell of the escaping gas, and the colour of its flame when ignited. The composition of phosphoretted hydrogen is expressed by the formula PH₃.

Touch a fragment of dry phosphorus with a glass rod which has been heated till it feels warm to the hand. Note that even at this moderate temperature the phosphorus ignites, clouds of oxide of phosphorus being produced. Hold another freshly cut fragment on the point of a penknife. Note that, without ignition, oxidation is proceeding. Examine it in the dark. Note that this slow oxidation is accompanied by *phosphorescence*.

On account of its ready combustibility, phosphorus is used on the heads of lucifer matches to promote their ignition. A mixture of phosphorus and nitre is employed which, being explosive, is ignited by mere friction. "Safety matches" are tipped with the oxidising agent, while the combustible substance, a mixture of amorphous phosphorus and the sulphide of anti-



mony, is smeared on the box. To ignite such matches, the match must, therefore, be rubbed on the box. Amorphous phosphorus is an allotropic modification of phosphorus not spontaneously inflammable. It is formed when phosphorus is heated to 240° C. in absence of air.

Fill a dry bell jar resting on a dry plate with dry oxygen gas (supplied), and insert a deflagrating spoon containing some ignited dry phosphorus. Note the formation of white phosphoric anhydride. Collect this on a spatula and plunge into cold water.

What evidence is there of chemical combination? Note the formation of transparent glacial phosphoric acid, P_2O_5 , H_2O or HPO_3 . Boil the mixture for some time. A solution of ordinary phosphoric acid, P_2O_5 , $3H_2O$ or H_3PO_4 , will thus be obtained. Note that the solution is sour in taste and acid to litmus. Neutralise a little with caustic soda, and evaporate to obtain crystals of the soluble phosphate of sodium.

Place 10 c.c. of the phosphoric acid solution, previously largely diluted, in a small flask and run in lime water from a burette, constantly shaking the flask, until the precise point is reached when the precipitate at first formed no longer redissolves. Note the quantity of lime water used (x c.c.). Test the phosphate solution with litmus, and note that it is nearly neutral.

Place 10 c.c. of the diluted acid in another flask, and run in lime water, constantly shaking, until, after filtering, no further precipitate is produced by the addition of more lime water. Note that the quantity of lime used is rather more than double that required by the first experiment (2x c.c.). On testing with litmus the liquid will be found to be still neutral.

Into a third flask run three times the quantity of lime water used in the first experiment (3x c.c.), and, having filled the burette with the diluted phosphoric acid, run it into the lime water, with constant shaking, until, after filtering, the liquid ceases to be alkaline, and becomes just neutral. Note that approximately 10 c.c. of the acid have again been used.

There are obviously three stages in the reaction between phosphoric acid and lime, corresponding to the formation of three distinct compounds which may be expressed thus:—

$$\begin{split} &P_2O_5._3H_2O + CaO = P_2O_5._2H_2O.CaO + H_2O\\ &P_2O_5._3H_2O + _2CaO = P_2O_5.H_2O._2CaO + _2H_2O\\ &P_2O_5._3H_2O + _3CaO = P_2O_5._3CaO + _3H_2O \end{split}$$

and of these the first compound is clearly the only one soluble in water. The three compounds are distinguished as mono-

calcic, dicalcic, and tricalcic phosphate. The two first are acid salts, i.e. compounds intermediate between a salt and an acid, and either can be produced by mixing the other with the acid or the neutral salt, as the case may be, in the right proportion. If the solution of monocalcic phosphate be mixed with the liquid containing the precipitate of tricalcic phosphate, and allowed to stand, the dicalcic phosphate will in time be formed.

Many other acids are able to convert the insoluble phosphates into the soluble monocalcic phosphate. To one portion of the milky liquid add a few drops of dilute sulphuric acid; note that the precipitate dissolves. Add potash or lime water; note that it is reprecipitated. Through the other pass a stream of carbonic acid gas (supplied); again note that the precipitate dissolves, and is reprecipitated by potash. Write an equation to represent the action of sulphuric acid on phosphate of calcium.

Phosphoric acid is distinguished by two characteristic insoluble compounds: the phospho-molybdate of ammonium and the double phosphate of ammonium and magnesium. Take a few drops of one of the liquids containing phosphate of calcium, dissolve the precipitate by a drop of nitric acid, and add the liquid to a solution of molybdate of ammonium (the ammonium salt of the acid derived from the higher oxide of the metal molybdenum) contained in a test-tube. On warming, a characteristic yellow precipitate will be formed. To a small portion of the solution of phosphoric acid add a mixture of sulphate of magnesium, chloride of ammonium, and ammonia solutions. A characteristic white crystalline precipitate of the double phosphate will be deposited.

In the latter test ammonia is added to neutralise the acid, as otherwise no precipitate would be formed; the ammonium chloride must then be also added in order to prevent the precipitation of magnesia from the magnesium sulphate, a double salt of ammonium and magnesium being produced, from which magnesia is not precipitated by ammonia. This reaction is also used for the detection of magnesium; for this purpose, ammonia, ammonium

chloride, and sodium phosphate solutions are added to the liquid to be tested. A white crystalline precipitate shows the presence of magnesium in the solution.

Phosphates and Phosphatic Manures.—Phosphates occur very abundantly in nature. Bones contain phosphate and other salts of calcium (in addition to gelatine and fat), and "bone earth," the white ash left when bones are burnt, chiefly consists of phosphate and carbonate of calcium. Peruvian guano, the product of the partial decay of sea-birds' excrements, chiefly consists of phosphate of calcium mixed, when the guano occurs in rainless districts where the moisture is insufficient for complete putrefaction and nitrification, with phosphate and urate of ammonium. The coprolites found in Suffolk and Cambridgeshire chiefly consist of phosphate of calcium. Canadian appatite is a double phosphate and chloride of calcium.

The phosphorus required by plants is absorbed from the soil in the form of soluble phosphates, these being slowly formed by the action of the carbonic and other acids of the soil and of the acids in the root sap upon the insoluble phosphates. The soil is, however, frequently deficient in "available," i.e. easily soluble, phosphates, and phosphatic manures are then required. Now tricalcic phosphate as it occurs in bones, coprolites, appatite, and phosphatic guano (i.e. guano containing little or no combined nitrogen) is only very slowly dissolved by the weak acids existing in the soil, even when in a fine powder, and it is usual, therefore, previously to convert into soluble phosphate by sulphuric acid. The "superphosphate of lime" thus produced is a mixture of monocalcic phosphate and gypsum for

 $Ca_3 2PO_4 + 2H_2SO_4 = CaH_4 2PO_4 + 2CaSO_4$.

The substances produced are known as "dissolved guano," "dissolved bones" or "bone superphosphate," and "mineral superphosphate," according to their source.

When the monocalcic phosphate has been used as a manure and has been washed into and diffused through the soil by rain, it "reverts" into the insoluble dicalcic phosphate owing to the action of the bases of the soil. This being deposited in a fine state of division is easily redissolved, and it is therefore "available" for plant food. The fact that nitrogenous guano contains phosphate of ammonium renders this manure especially valuable, for this soluble phosphate is a neutral salt and therefore does not so easily "revert" in the soil into an insoluble form. "Reversion" is also noticed when superphosphate of lime is kept for some time, for the monocalcic phosphate reacts with unchanged tricalcic phosphate in the manure yielding the intermediate dicalcic phosphate.

Iron made from Cleveland iron ore contains a large amount of phosphide

of iron. To convert this into steel, the phosphorus is oxidised by a current of heated air blown through the molten metal in contact with excess of lime. An unstable basic phosphate of lime, * Ca₃2PO₄·CaO, is thus produced which, when finely ground to an impalpable powder, constitutes "basic slag," a substance which can be easily dissolved by weak acid, and is therefore "available" as plant food. As this is a basic substance, it must not, when used as a manure, be mixed with nitrogenous guano or sulphate of ammonia, as ammonia gas would be set free and lost. Similarly "superphosphate of lime" must not be kept mixed with nitrate of soda, as, being an acid phosphate, it sets free nitric acid which, owing to the heating of the mass, is volatilised.

XXIV. SILICA: SAND AND CLAY

Potassium and sodium have been found to be the most oxidisable of all the metals examined. So great is their greediness for oxygen that the oxides of almost all elements are attacked by them, potash or soda being formed and the element set free. This reaction may be employed for preparing the element silicon from its oxide silica. Heat some silver sand (nearly pure silica) in a test-tube with a little sodium. Note that a brown non-metallic substance, the element silicon, is liberated. It has been found by experiment that silica contains 46.6 per cent. of silicon and 53.3 per cent. of oxygen. What is the simplest formula that represents its composition?

Mix together 20 grams of silver sand with twice its weight of caustic soda, and heat the mixture strongly on a clean iron dish over a hot fire. When steam ceases to be given off and action appears to be complete, allow the liquid mass to cool, lixiviate with water, boil, and then filter the solution of *silicate of sodium* produced. Evaporate a part of the solution till a thick syrupy residue of "soluble glass" is obtained.

^{*} A basic salt is a compound intermediate between a base and a salt, just as an acid salt is intermediate between an acid and a salt.

Take two other portions of the solution, and dilute one of them with ten times its bulk of water. Now add diluted sulphuric acid (1 to 4) to each portion. Note that no change occurs in the weak solution, the silicic acid, so far as it is replaced by sulphuric acid in the sodium salt, remaining dissolved, but that from the strong solution white gelatinous silica is deposited, the silicic acid set free being unstable. (Compare this action with that of dilute sulphuric acid on weak and strong solutions of sulphite of sodium.) Evaporate the weak solution containing silicic acid to dryness on the water bath; note the white residue of silica left. Add water and hydrochloric acid; note that in both it is insoluble. experiments show that silicic acid is a very unstable compound, easily decomposing into silica and water; and that silica, unlike most anhydrides, is insoluble in water and incapable of recombining with water to form silicic acid. They also provide a method for distinguishing silicic acid or the silicates, as no other substance would yield a white gelatinous precipitate when hydrochloric acid is added to its solution, or a white residue, insoluble in water and acid, when the acid mixture is evaporated to dryness.

Silica, the oxide of the element silicon, is the most abundant constituent of the earth's crust. It occurs uncombined as quartz, sand, and flint, minerals which, though geologically different, are chemically identical. Silica also occurs combined with bases. Felspar and mica, two minerals which, mixed with quartz, constitute granite, are double silicates of aluminium with either calcium, magnesium, potassium, sodium, or iron, while clay, produced by the weathering and consequent disintegration of felspathic rocks, is essentially silicate of aluminium, still retaining, however, variable quantities of the other silicates. Both clay and sand are usually coloured yellow, brown, or red, due to the presence of ferric oxide. Asbestos is a basic silicate of calcium and magnesium; meerschaum and steatite (talc, soapstone, or french chalk) are acid silicates of magnesium.

Like phosphoric anhydride silica combines with water and bases in more than one proportion. Silicate of sodium has the formula Na₄SiO₄ (that is, SiO₂.2Na₂O), and with this the soluble silicic acid probably corresponds, H₄SiO₄ 'or SiO₂.2H₂O). But the silicates occurring in nature more often

correspond to the acid H_2SiO_3 (that is, $SiO_2.H_2O$). Thus a silicate of calcium that occurs naturally is $CaSiO_3$ (or $SiO_2.CaO$). China clay or kaolin, a nearly pure silicate of aluminium, is $2AlHSiO_4.H_2O$ (or $2SiO_2.H_2O.Al_2O_3$; H_2O).

Dilute a little of a weak solution of silicate of sodium with water, and add a few drops of solution of alum. Note that the liquid is rendered turbid with a gelatinous precipitate of hydrated silicate of aluminium (clay). Make a mixture of clay and distilled water, and divide into two parts. To one add distilled water and to the other lime water. Note that in the latter the clay becomes granular and separates from the liquid; in the other the clay remains suspended.

To a portion of the strong solution of silicate of sodium add a saturated solution of alum. Note that a solid jelly of hydrated silicate of aluminium is formed. Heat the jelly on a dish on the water bath. Note that the anhydrous silicate of aluminium produced is porous and no longer gelatinous. Wash the mass well with water. Then heat a little on the loop of a platinum wire in the Bunsen flame. Note that it is infusible.

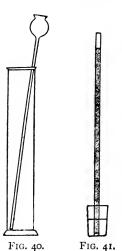
Owing to these properties clay is used as the principal ingredient in pottery and porcelain. Vessels made of pure clay are, when baked, porous and friable. The clay is therefore mixed with a little fusible silicate, for instance, silicate of lime, which, in the baking, penetrates into the pores of the clay. The glaze on the surface is also produced by covering with a fusible silicate. Bricks are made from "brick earth," a mixture of clay and sand in such proportions that the bricks bake to a solid mass without cracking and warping. Tiles are made from a purer clay, as they need to be less porous than bricks; being thinner, they can be more easily baked.

Mix a very little of the syrupy silicate of sodium with a trace of lime and fuse by means of a blow-pipe on the loop of a platinum wire. Note that a bead of glass is produced. Dip such beads into solutions of salts of manganese, chromium, and cobalt, and heat again. Note the different colours imparted to the beads—amethyst, green, and blue.

The Bohemian glass used for chemical apparatus consists of silicates of potassium and calcium, window or crown glass of silicates of sodium and calcium, flint or crystal glass of silicates of potassium and lead, and bottle glass of silicates of sodium and calcium and some iron and aluminium. Glass containing sodium or lead is "soft" and easily fusible, that containing potassium and calcium is "hard" and infusible.

The Soil and its "Mechanical" Properties.—Soil essentially consists of sand and clay in varying proportions, mixed with more or less gravel, chalk, and decaying vetegable matter ("humus"). The "mechanical

analysis," i.e. the determination of the proportion of gravel, sand, and clay, may be roughly carried out as follows:-From a known weight of air-dried soil, sift out the gravel and weigh it. Mix the sifted soil thoroughly with water, and pour the mixture into a wide tall cylinder (Fig. 40). allow a very slow, steady stream of water to run into the bottom of the cylinder, gently stirring the contents from time to time with the tube through which the water is passing, and so arrange the supply of water that the clay and very fine sand are washed away. When thoroughly washed, dry the residue and weigh it. The quantity of clay and fine sand is determined by difference. Express the result as percentage of (1) gravel, (2) coarse sand, (3) clay and fine sand. Upon the proportion of sand and clay mainly depend the dryness or wetness of a soil. This is due, firstly, to the greater porosity of sand, and secondly, to the greater capillarity of clay.



If sandy and clayey soils be percolated with water (Fig. 16), the water will pass through the sandy soil more quickly, because the particles are coarser, and the spaces between therefore larger. The sandy soil is, in fact, more porous. The gelatinous nature of the hydrated silicate of alumina constituting clay, also renders clayey soils less porous. If such a soil be "burnt," the anhydrous silicate is produced, and the soil is rendered more porous. The same effect will be produced by the application of lime, which renders the gelatinous clay more granular. (See above.)

If two long glass tubes, filled with the two soils, previously thoroughly dried and disintegrated, be allowed to stand in vessels of water (Fig. 41),

the water will ultimately rise higher in the tube of soil consisting of the smaller particles. The attraction which solids have for liquids is manifested in the rise of liquids in small tubes, and it is therefore called "capillary attraction." It is, however, simply dependent upon the amount of surface the solid exposes to the liquid; and as small particles present more surface than large particles in proportion to their bulk, and the interspaces between are smaller, the capillarity of a clay soil is greater than that of a sandy soil. It is for this reason that clayey soils have more power than sandy soils of sucking up moisture from below, and therefore remaining moist in dry weather.

The cooling effect of moisture on soils, and the action of frost on soils,

have been referred to on pp. 34, 35.

XXV. CARBON: MARSH GAS

HEAT strongly in separate test-tubes (1) a piece of wood and (2) a piece of bone. Note that in each case charring occurs owing to the decomposition of the organic matter, and that finally black masses of (1) vegetable charcoal and (2) animal charcoal are left, which, while they have retained the form of the pieces of wood and bone used, are much lighter in weight, having become porous. If the combustible portion of the wood charcoal and "bone-black" be burnt off by kindling and then placing in bottles of oxygen, it will be found that the gas produced in each case renders lime water milky, and is therefore carbonic acid gas, and that in each case also, a white ash, "wood ashes," and "bone ash," is left. Both kinds of charcoal, in fact, consist of the element carbon, together with the mineral substances of the wood or bone from which the charcoal is made.

Like sulphur and phosphorus, carbon exists in both crystalline and amorphous modifications. Diamond, distinguished by its lustre, and hence valuable as a precious stone, and by its extreme hardness, is a nearly pure and colourless crystalline modification of carbon. Graphite

(plumbago or black lead), distinguished by its softness, and hence used as a writing material, is a black modification also capable of existing in a crystalline form. The carbon of (1) animal and vegetable charcoal; (2) lamp-black, the soot produced by the incomplete combustion of oils burning with a smoky flame; (3) coke, the residue of the destructive distillation of coal in the manufacture of coal gas; and (4) gas carbon, the deposit in the upper parts of the retorts used for the same purpose, is the black amorphous modification. "Charcoal burning," the process by which wood is converted into charcoal, once an important industry, is still carried on in woodland districts. Stacks of wood are set fire to, but by covering the stacks with earth or turf the supply of air is so limited that the wood is carbonised, but not burnt.

The wood ashes, produced by the complete combustion of wood, have a high value as a fertiliser, owing chiefly to the large quantity of carbonate of potassium they contain. When lixiviated with water, and the solution evaporated to dryness, a residue of impure carbonate of potassium is obtained, constituting, when calcined, the pearl-ash of commerce.

The attraction that exists between liquids and the surface of solids has been already referred to (p. 102). Charcoal exhibits this attraction in an extraordinary degree. Render some water blue with solution of litmus, and shake with some powdered animal charcoal for a few minutes. Now throw upon a filter. Note that the filtrate is colourless, the dissolved colouring matter having adhered to the charcoal.

This force of adhesion is also exerted between solids and gases, and its extent will largely depend upon the amount of surface exposed by the solid. Owing to its porousness, wood charcoal presents an enormous surface, and exhibits an enormous power of absorbing gases. Heat a lump of wood charcoal in a tube to bright redness, so as to expel absorbed gases, cork the tube, and allow to cool. When cold, counterpoise on the pan of the balance, then remove the cork, and watch the gradual increase in weight. Place a small lump of charcoal in a flask of water. Note that it swims on the surface. Now boil the water till the air has been expelled from the pores of the charcoal. Allow to cool, and notice that the density of charcoal, when free from air, being greater than water, the lump sinks.



FIG. 42.

Fill an inverted tube with ammonia gas (supplied) by mercury displacement, and insert a lump of charcoal previously heated to redness (Fig. 42). Note the almost complete absorption of the ammonia.

Owing to its power of absorbing gases, wood charcoal is used as a deodoriser of sewer gases, etc. Not only does it absorb noxious emanations, but, by condensing them in its pores in close contact with the atmospheric oxygen, also absorbed, it oxidises and disinfects them. As a rule, the more condensible and soluble a gas, the more is it absorbed. Owing to its power of adhesion to dissolved

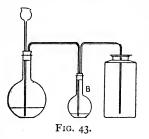
solids, animal charcoal is used as a decoloriser; for instance, in sugar refining. Blocks of animal charcoal are also employed as the filtering medium in water filters, and, when fresh, serve to remove, and perhaps oxidise, the microscopic living organisms in the water.

When organic matter decays, or when submitted to destructive distillation, a compound is produced of carbon and hydrogen. The bubbles of gas that rise from decaying vegetable matter at the bottom of stagnant pools chiefly consist of this compound, which has therefore received the name of "marsh gas." It also constitutes the "fire-damp" in coal seams, to which explosions in coal mines are generally due. Heat some wood in the flask of the apparatus figured on p. 86. Immerse the U tube in a beaker of cold water in order to condense the creosote and other liquid products of distillation, and collect the gas evolved in inverted test-tubes or cylinders over water. Preserve the U tube and its contents for future examination. Apply a light to the gas in one of the cylinders, and observe that it is combustible, and burns with a flame somewhat bluer than hydrogen, and slightly luminous. By the usual methods it can be shown that pure marsh gas produces carbonic acid gas and water when burnt, and therefore is a compound of carbon and hydrogen; but, produced as above, the gas is not pure, but is mixed with free hydrogen, and with other compounds of carbon. Pure marsh gas has been found by experiment to contain 75 per cent. of carbon, and 25 per cent. of hydrogen. Calculate the simplest formula that would represent its composition.

XXVI. THE OXIDES OF CARBON

It has been found that when carbon burns in air or oxygen, the dioxide of carbon or carbonic acid gas, CO₂, is formed. The gas was found to be an acidic oxide, dissolving in water to form a liquid acid to litmus, and combining with lime to form chalk, which is therefore carbonate of lime. As this compound is a gas, it should be possible to prepare it by the action of a less volatile acid upon a carbonate (see p. 77).

Fit up the apparatus figured. In the large flask place some lumps of chalk or, better, marble. Pour in some water and then a little hydrochloric acid. Wash the gas by passing it through a flask containing water. Collect the gas by downward displacement of air. Test it with a taper, blue litmus solution, and lime water. Is it identical with that

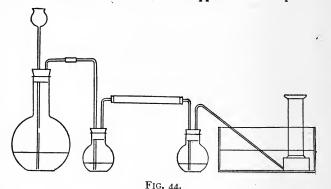


obtained by the combustion of carbon? Determine its relative density by means of the apparatus figured on p. 13. For this purpose, the gas must be dried by passing it through a U tube containing pumice soaked with oil of vitriol attached to the flask B.

Although carbonic acid gas does not support the combustion of a taper, it may be capable of losing oxygen to other

combustible substances, and therefore of supporting their combustion. Ignite a piece of magnesium and plunge it into a bottle of the gas. Note that the magnesium continues to burn, although apparently with some difficulty; that the white oxide, magnesia, is produced, together with a black substance Pour a little hydrochloric acid into the bottle to dissolve the magnesia, filter off the black particles, wash with water, and dry. Heat the black substance in a dry test-tube. Does it burn and produce carbonic acid gas? If so, it is carbon. Represent the reaction by an equation.

Carbonic acid gas even supports the combustion of carbon itself. Attach the carbonic acid apparatus to a piece of



combustion tubing, flask, and bent tube, as figured. Fill the combustion tube with lumps of dry charcoal, and place a solution of caustic potash (r gram to 3 c.c. of water) in the flask through which the products of combustion pass. Heat the combustion tube strongly, and then pass a very slow current of carbonic acid gas through the apparatus. Note that the gas after passing over the heated charcoal is no longer completely absorbed by the caustic potash, as would be the case if the carbon dioxide were unchanged. Collect some

over water made alkaline with caustic potash. Does it now turn blue litmus red and render lime water milky? Is it combustible? Is carbonic acid gas the product of combustion? Observe that the charcoal in the tube has slowly burnt away.

The only possible explanation of this change is that the carbon burns in the carbon dioxide, producing a lower oxide of carbon. This lower oxide has no action on litmus or on bases, and is therefore not an anhydride; but it burns in the air, producing carbonic acid gas. Analysis shows that its composition is represented by the formula CO; it is therefore the monoxide of carbon, and has been produced thus:—

$$CO_2 + C = 2CO$$
.

This experiment explains the occurrence of a blue flame over a coke fire. The coke burns without flame at the bottom of the fire to carbonic acid gas, but this, on passing over more heated coke, is reduced to carbon monoxide, which burns at the top of the fire with a blue flame to carbon dioxide. In a slow combustion stove, where insufficient air is supplied for complete combustion, the carbon monoxide escapes unburnt. As this gas is very poisonous, care must be taken that no leakage occurs from the flues of such a stove into the room. "Producer gas" is the product of the action of air on excess of coke, and consists of carbon-monoxide and nitrogen. "Water gas" is the product of the action of incandescent coke on steam,— $H_2O+C=CO+H_2$,—and therefore consists of a mixture of carbon monoxide and hydrogen. Both these mixtures are largely used as fuels.

Besides reducing carbon dioxide, charcoal can also be employed to reduce the metallic oxides. Mix a little litharge with sodium carbonate, and place the mixture in a small hollow on a lump of charcoal. Now heat the mixture by means of a mouth blow-pipe flame, so regulating the air that the flame directed upon the mixture is luminous. Such a flame contains free carbon, which assists the reduction. Note that in a few minutes globules of metallic lead are produced. Mix together a little oxide of arsenic and powdered charcoal. Place the mixture at the bottom of a very small bulb tube made of a

piece of glass tubing, and heat. Note the deposit of arsenic formed upon the sides of the tube.

Owing to this power of carbon as a reducing agent, it is used in metallurgy. Generally speaking, the metallic ores are roasted to convert the sulphide, hydroxide, or carbonate of the metal, as the case may be, into oxide, and then heated with charcoal, coal, or coke, either with or without a fusible compound to act as a flux, until the oxide is reduced to the metal. Iron, copper, antimony, manganese, tin, zinc, sodium, and potassium, are all separated from their oxides by reduction by carbon. In some other cases, e.g. magnesium, which is obtained from its chloride, the metal sodium is used as a reducing agent, while in the case of lead and mercury, which are obtained from their sulphides, no reducing agent is necessary, careful roasting serving to burn off the sulphur as sulphur dioxide. Aluminium is obtained by the electrolysis (i.e. decomposition by electricity) of fused cryolite, a native double fluoride of aluminium and sodium.

XXVII. THE CARBONATES

DETERMINE the proportion of lime and carbonic acid gas in chalk. Into a weighed capsule provided with a lid place about 2 grams of pure chalk, dry by warming in the hot water oven for a few minutes, cool in a dessicator, and weigh. Now heat to a full red heat until no further loss in weight occurs, then cover the capsule, cool in a dessicator, and weigh again. From the resulting weight of lime find the percentage composition of chalk, and express this by the simplest formula possible. Calculate what weight of quicklime should be obtained by burning 100 tons of chalk in a kiln. What weight of slaked lime would this produce?

Carbonates occur abundantly in nature: thus magnesian limestone is carbonate of magnesium; dolomite is a double carbonate of calcium and magnesium; malachite is a double carbonate and hydroxide of copper; calamine is the carbonate of zinc; clay ironstone is the carbonate of iron.

But by far the most abundant is the carbonate of calcium. This occurs in chalk, limestone, marble, calc-spar, etc., substances which, though geologically different, are chemically identical, and consist of the nearly pure carbonate. From these minerals lime is obtained by "burning" in kilns, i.e. by heating the carbonate by means of burning fuel, either placed beneath it or mixed with it to dissociate it into lime, which remains in the kiln, and carbonic acid gas, which escapes into the air. (Dissociation is reversible decomposition. Thus the decomposition of chalk is dissociation because the lime and carbonic acid gas recombine at a lower temperature. The decomposition of red oxide of mercury is another instance of dissociation, the chemical change being reversible.)

Mortar and Cements.—Mortar is prepared by slaking quicklime, adding enough water to make into a paste, and mixing with three or four times its weight of sharp sand. It "sets" in a few days owing to evaporation of water, and gradually increases in hardness owing to absorption of atmospheric carbon dioxide and the formation of chalk. Portland and Roman cement are prepared by grinding mixtures of chalk and clay (or river mud) with water, drying the mixture, "burning" in kilns, and powdering. Unlike mortar, these cements, after mixing with water, have the power of setting under water, and are therefore called "hydraulic mortars." The setting is due to the power of absorbing water possessed by both quicklime and anhydrous silicate of aluminium and the production of solid hydrates. The dissolved carbonic acid in the water is also gradually absorbed.

If the foregoing determination shows that carbonate of calcium is a compound containing lime and carbonic acid gas in single combining proportions, it may be supposed that the carbonate of sodium or potassium has a similar composition. With a view to determine this, try whether these carbonates are decomposed by heat, by heating strongly in test-tubes. If, unlike the carbonates of other metals, those of the alkali metals prove to be incapable of dissociation by heat, the method of titration with an acid, using litmus as an indicator, can be employed; for soluble carbonates are, unlike most salts, strongly alkaline to litmus.

Weigh out two portions of pure carbonate of sodium, say I gram each, into two flasks, dissolve in distilled water, render

blue with solution of litmus, and titrate with the dilute sulphuric acid of known strength. Use all the precautions described on p. 71, being particularly careful to boil off the carbonic acid gas set free, as this, while in solution, is acid to litmus. Having obtained concordant results, calculate from the sulphuric acid employed the amount of sodium in the carbonate of sodium taken (remembering that sulphate of sodium has the formula Na₂SO₄). Does it correspond with the formula Na₂CO₃, and if so, do the proportions of carbonate of sodium and sulphuric acid used correspond with the equation:—

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

Although carbonic acid gas is only slightly soluble in water under ordinary atmospheric pressure, there is evidence that it does combine to form an unstable carbonic acid, $H_2O.CO_2$ or H_2CO_3 . Thus its solution is acid to litmus, and a bottle of aerated water, *i.e.* water charged with carbonic acid gas under pressure, does not immediately lose all its excess of the gas when opened, but the bubbles keep rising to the surface, especially when the liquid is agitated or warmed, for a considerable time, indicating that the acid is only slowly decomposed into its anhydride and water. In its instability, carbonic acid resembles silicic acid and sulphurous acid.

Special attention must be drawn to the fact that carbonates neutralise acids like free bases. The statements with respect to the use of lime in promoting nitrification in the soil (p. 93) will therefore hold good for chalk. Again, with regard to the incompatibility of manures, to mix chalk with "superphosphate of lime" would be as undesirable as to mix lime with it.

Through some lime water pass a current of carbonic acid gas. Note that the precipitate of chalk first formed gradually disappears, and a clear solution is at length obtained. Heat a portion of the clear liquid. Note that bubbles of carbonic acid gas are set free, and simultaneously the chalk is precipitated. To another portion add some lime water, and note that this also precipitates chalk. The simplest explanation of these reactions is that a soluble acid-carbonate of calcium is formed,

which is decomposed by heat, and acted upon by lime, as represented in the equations:—

 $\begin{aligned} &\text{CaCO}_3 + \text{H}_2\text{CO}_3 = \text{CaH}_2\text{2CO}_3 \\ &\text{CaH}_2\text{2CO}_3 = \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \\ &\text{CaH}_2\text{2CO}_3 + \text{Ca2OH} = 2\text{CaCO}_3 + 2\text{H}_2\text{O}. \end{aligned}$

Hardness of Water.—Although the acid carbonate of calcium has, owing to its instability, never been isolated, the acid carbonates or "bicarbonates" of sodium and potassium are well-known and stable salts. (These are produced by passing carbonic acid gas into cold saturated solutions of the carbonates; they are decomposed into the carbonate and carbonic acid when warmed.) There is therefore good reason to believe that the calcium compound can also exist in solution. Its probable existence affords an explanation of the hardness of spring water which prevents the lathering of soap until all the lime has been deposited as a curd. water deposits its chalk on the sides of the kettles or boilers in which it is heated in the form of "fur"; hence, when the hardness is due to dissolved chalk, it is said to be "temporary." To soften such water on a large scale, lime may be placed in the reservoirs used for storing it. The hardness of spring water may also be due to dissolved sulphates or chlorides of calcium and magnesium, especially the sulphate of calcium. are, of course, not precipitated by boiling, and the hardness they produce is said to be "permanent." To soften such water on a small scale, carbonate of sodium may be added, which, in absence of dissolved carbonic acid, completely precipitates the lime or magnesia as carbonate, thus:-

$$Na_2CO_3 + CaSO_4 = Na_2SO_4 + CaCO_3$$

As already pointed out on p. 30, spring water obtains its dissolved salts from the soil or rock strata through which it passes. Owing to the carbonic acid in rain water, much of the chalk contained in spring or river water is dissolved from the soil, a fact that explains the necessity of the application of lime or chalk every few years on most land.

The only other carbonate that need be examined is the carbonate of ammonium. Procure a specimen of "lump ammonia." Notice that it smells strongly of ammonia, showing that even at the ordinary temperature it dissociates into ammonia and carbonic acid. Dissolve a little in water, and to the solution add a solution of gypsum. Note that chalk is precipitated:—

 $(NH_4)_2CO_3 + CaSO_4 = (NH_4)_2SO_4 + CaCO_3$

Now mix some dry sulphate of ammonium and chalk together, and warm the mixture. Note that ammonia is evolved. On testing the residue it will be found to contain gypsum. Hence the reverse change has now occurred, and—

$$(NH_4)_2SO_4 + CaCO_3 = (NH_4)_2CO_3 + CaSO_4$$
.

Explain why, under different conditions, the reaction should be reversed.

Both these reactions are of agricultural importance. When, from a fermenting manure heap, ammonia is found to be escaping, it is customary to sprinkle the heap with gypsum to "fix" the ammonia, in accordance with the first reaction. The occurrence of the second reaction shows the inadvisability of mixing together a salt of ammonia with any substance containing chalk previous to its application as a manure.

XXVIII. CONCLUSIONS

In Part I. it was observed that, in the case of certain oxygen compounds, the elements were united in unalterable proportions. In Part II. this observation has been extended to so large a number of other compounds of various elements that it may be stated as a primary law of chemical combination that elements unite in definite proportions by weight. These proportional weights, compared with hydrogen as unity, are termed the combining weights of the elements.

It has, however, been noticed that elements frequently unite in more than one proportion by weight, and it is consequently difficult to assign fixed combining weights. There is, however, always a simple relationship between the proportions, so that, taking one of the proportions in which each element enters into combination as the combining weight, it may be stated as a second law of chemical combination, that *elements unite in the*

proportion of their combining weights, or in simple multiples of these weights.

It has been found possible to derive the probable composition of a compound of two elements, by the proportion in which each unites with a third. In other words, two elements usually unite with a third in the proportion in which they unite with each other. In the case referred to, a fourth element was introduced, thus:—

Lead unite	es with	oxygen in	the prop	ortion of	206 : 16
Oxygen	"	hydrogen	"	"	16:2
Hydrogen	22	chlorine	,,	"	2:71
Therefore,					
Chlorine	>>	lead	**	,,	71:206



FIG. 45.

To explain these facts of chemical combination, it is conceived that when elements combine, it is their ultimate particles or atoms that unite with each other, and that the relative weights of these atoms are the combining weights of the elements. Thus, if the weights of atoms of oxygen and nitrogen be 16 and 14 times respectively the weight of an atom of hydrogen, oxygen and nitrogen will combine in the proportion of these weights, or in simple multiples of them.

The laws of chemical combination have been found to hold good for compounds as well as elements. Thus, hydrochloric acid combines with ammonia in definite proportions. There is physical evidence that of both elements and compounds there are ultimate particles or *molecules* indivisible, without altering their nature. A molecule of hydrochloric acid must

be a compound of atoms of hydrogen and chlorine, a molecule of ammonia must be a compound of atoms of hydrogen and nitrogen, and the weight of each must be the sum of the weights of its component atoms. If, then, the weight of a molecule containing an atom of hydrogen and an atom of chlorine be 36.5 times the weight of an atom of hydrogen, and the weight of a molecule containing three atoms of hydrogen and one atom of nitrogen be 17 times that of an atom of hydrogen, the proportions in which hydrochloric acid and ammonia will combine will also be 36.5:17. This was found by experiment to be the case.

The relative densities of four gases have been determined. It is noticeable that the ratio of the relative densities of the two compound gases, ammonia and carbon dioxide, is also the ratio of the calculated molecular weights:—

	Relative Density.		Molecular	
	Air = I	Hydrogen=1	Weight.	
Ammonia	.589	8.5	17	
Carbonic acid gas	1.524	22	44	
Hydrogen	.069	I	(2)	
Nitrogen	.970	14	(28)	

This is found to be true of other volatile compounds, and can only be explained by supposing that equal volumes of gases contain an equal number of molecules (Avogadro's hypothesis). Now the molecular weights of ammonia and carbon dioxide are exactly double the densities compared with hydrogen as unity; and the relative densities of all gases being as the molecular weights, it follows that the molecular weights of all other gases must be double their relative densities. There is abundant reason for believing that Avogadro's hypothesis holds good for gaseous elements as well as gaseous compounds. This being so, the molecular weights of hydrogen and nitrogen must be 2 and 28 respectively, and therefore double the atomic

weights, or, in other words, the molecules of hydrogen and nitrogen must each contain two atoms (H₂ and N₂).

This observation that the relative density is always half the molecular weight is of use in determining the molecular composition of volatile substances. For instance, nitric oxide might have the composition represented by either of the formulæ NO and N₂O₂. But the relative density is found by experiment to be 15. Hence the molecular weight is 30. and this corresponds with the formula NO. It also makes it possible to calculate the weight of any volume of gas, if the molecular weight be known, from the weight of a liter of hydrogen (=.0896 grams when measured at o° C. and 760 m.m.). For instance, the calculated molecular weight of ammonia (NH₂) is 17. The weight of a liter of ammonia gas at o° and

760 m.m., will therefore be $\frac{.0896 \times 17}{2} = .7616$ grams.

In the foregoing studies it has been observed that the nonmetallic elements form compounds with hydrogen. These substances differ in their composition:-

Hydrochloric acid	HCl	Hydrobromic acid	HBr
Water	H_2O	Sulphuretted hydrogen	H_2S
Ammonia	NH_3	Phosphoretted hydrogen	PH_3
Marsh gas	CH_4	Silicon hydride	$\mathrm{SiH_4}$

Those elements which combine with one, two, three, and four atoms of hydrogen are termed, respectively, univalent, bivalent, trivalent, and quadrivalent. The metallic elements have less tendency to combine with hydrogen, but they combine with chlorine, which is univalent; and they combine with oxygen and sulphur, which are bivalent; so that their valency is easily determined. Thus, sodium and potassium are univalent, for they form the compounds Na'Cl', K'Cl', Na, O" and K, O". Calcium, barium, magnesium, zinc, lead, copper, and mercury are bivalent, for they form the compounds Ca"O", Ba"Cl₂', Mg"Cl₂', Zn"O", Pb"O", Cu"S", Hg"O". Aluminium appears to be trivalent, for it forms the compound Al₂"O₃". Frequently the elements have more than one valency, for iron forms ferrous and ferric chlorides, Fe"Cl₂' and Fe" Cl₃'. Groups of elements act like elements. Thus NH₄, OH and NO₃ are univalent like K and Cl, forming (NH₄)'Cl', Na'(OH)' and H'(NO₃)'; CO₃ and SO₄ are bivalent, forming Na₂'(CO₃)" and Ca"(SO₄)"; PO₄ is trivalent, forming H₃'(PO₄)"" and Ca₃"₂(PO₄)""; SiO₄ is quadrivalent, forming Na₄'(SiO₄)"".

This study of a few of the more important elements has shown that they fall into groups having certain properties in common. Of these groups may be mentioned potassium and sodium; calcium, strontium, and barium; zinc and magnesium; chlorine, bromine, and iodine; oxygen and sulphur; nitrogen and phosphorus. The properties common to the elements of each group are both physical and chemical, e.g. softness, density, oxidisability, solubility of salts, and valency, and therefore the composition of compounds. When three or more elements exist in a group, it is found that the properties vary as the atomic weights. Thus strontium has an atomic weight intermediate between those of calcium and barium; its properties, and the properties of its compounds, are also intermediate. Bromine has an atomic weight intermediate between those of chlorine and iodine; chlorine is a gas, iodine a solid, and bromine a liquid. When all the known elements are arranged in the order of their atomic weights, it is found there is a periodic recurrence of similar properties, so that if each period be placed one under the other, the elements fall into groups (the elements mentioned above are arranged as they arrange themselves in these groups); and it is possible even to foretell the properties of any element by its atomic weight, and the position it would therefore assume in relation to other elements. These facts are mentioned, because it should be realised that the reactions and properties of the substances studied in the foregoing pages are not haphazard, but the result of this periodicity of properties depending on the atomic weights.

QUESTIONS AND PROBLEMS FOR REVISION AND EXAMINATION.

BASIC OXIDES, ACID OXIDES, AND SALTS.

- I. How are the oxides of magnesium and potassium distinguished from the oxides of phosphorus and sulphur?
- 2. What happens when a solution of a basic oxide is exactly neutralised by a solution of an acidic oxide? Give examples.
- Define a basic oxide, an acidic oxide, and a salt, and give examples of each of these classes of chemical compounds.
- Give a method of distinguishing a metallic from a non-metallic element.
- 5. Is the element hydrogen a metal or a non-metal? Upon what fact do you base your answer?
- *6. Of the three powders, identify the acidic oxide, the basic oxide, and the salt. (Silica, magnesia, and gypsum.)

CHEMICAL PROPERTIES OF THE METALS: THE METALLIC OXIDES.

- 7. State two methods which may be employed to study the oxidisability of the metals.
- 8. Compare the action of air in the cold on sodium, potassium, magnesium, zinc, iron, copper, and mercury. Why does iron corrode so much more than zinc? What are tinned and galvanised iron?
- 9. Describe fully the action of sodium and potassium on water, giving the products of the reaction. In what respect does the action of sodium differ from that of potassium, and what does this teach as to the relative attraction of these two elements for oxygen?
- 10. State what are the colours imparted to a non-luminous flame by the incandescent vapours of sodium, potassium, calcium, strontium, and barium compounds. When the colour of potassium vapour is masked by that of sodium, how should the flame be viewed to render the former colour visible?
- Explain the use of the spectroscope for identifying the incandescent vapours of metals.
- 12. If in their oxidisability, calcium, barium, and strontium are intermediate between sodium and magnesium, what should be their behaviour towards air and water?
- 13. State whether magnesium, zinc, and iron are combustible, and under what conditions (if any) they attack water. Describe the experiments made upon the subject.

14. Under what conditions (if any) can copper, mercury, silver, gold, and platinum be oxidised? What experiment can you cite to show that heated copper has no action on steam?

15. Distribute the metals barium, calcium, copper, gold, iron, magnesium, mercury, potassium, sodium, strontium, and zinc, into five groups, and ascribe a name to each group.

16. What is meant by the terms "alkali" and "alkaline earth"? Why are gold and silver described as noble metals?

17. Give two or three instances of the grouping of metals holding good not only for oxidisability, but also for the solubility of the oxides, and for the specific gravity, fusibility, malleability and ductility, or conductivity of the metals.

18. Give an instance of metals of the same group occurring together in nature. What metals are found in the free state in nature? What are the minerals loadstone, hæmatite, emery, tinstone, and pyrolusite?

*19. To what group should the metal be ascribed, as judged by its

oxidisability? (Tin.)

*20. Identify the metal in the salt by the colour of its incandescent vapour. (Sodium, potassium, calcium, strontium, or barium.)

*21. Is the metallic oxide an "alkali," an "alkaline earth," or an "earth"? (Soda, potash, lime, baryta, magnesia, or oxide of zinc.)

THE METALS: THEIR PHYSICAL PROPERTIES.

- 22. What is an alloy? Is the property of forming alloys possessed by all the elements? Why are gold and silver alloyed with copper for purposes of coinage? Why are tin and lead alloyed for use as solder?
- 23. What do you understand by the malleability and ductility of metals? Name the most malleable and one of the most ductile of metals.
- 24. Are metals as a rule good or bad conductors of heat and electricity? Name two of the best conductors.
- 25. Give an instance of the expansion of metals by heat and its effect upon any structure or instrument.
- 26. Why should a mercurial thermometer be so sensitive to rapid changes of temperature?
- 27. Name a metal whose density is less than that of water, and a metal whose density is greater than mercury.
- 28. Name metals which are (1) liquid at the ordinary temperature, (2) fusible below 100°, (3) fusible below a red heat, (4) fusible at a red heat, and (5) only fusible at a white heat. If one metal be alloyed

with another, what is usually the effect upon the melting point? Give an example.

29. Name some soft and some hard metals. How may the relative hardness be roughly determined? What is the effect of 1 per cent. of carbon in iron upon its hardness, and how may steel be made harder or less hard by "tempering"?

COMBINING WEIGHTS OF THE ELEMENTS.

30. What evidence is there that the same compound always contains the same elements in the same proportions by weight? examples.

31. What evidence is there that two elements can combine in two or more proportions? In this case is there any simple relation

between the proportions?

32. What is meant by the "combining weights" of the elements, and with what are they compared as unity? What are the combining weights usually taken for hydrogen, oxygen, carbon, and mercury?

33. The proportion in which hydrogen and oxygen are combined in water is as 1:8, but the combining weight of oxygen is taken as 16 (hydrogen = 1). What number of combining weights then of hydrogen and oxygen are combined together in water, and what formula may be employed to express this shortly?

34. Carbon combines with oxygen to form carbonic acid gas in the proportion of 3:8. The combining weights of the elements are 12 and 16 respectively. Represent the composition of carbonic acid

gas by the simplest possible formula.

35. What does the formula "HgO" mean both as to the elements of the compound and their quantities?

36. For what elements do the following symbols stand: C, Cu, Fe, H, Hg, Mg, Mn, N, Na, P, Pb, K, S, and Si?

37. Determine the proportions in which silver and oxygen are combined together in the oxide of silver, after first drying in the water oven.

COMPOSITION OF THE BASIC OXIDES AND HYDRATES.

38. The composition of lime is expressed by the formula CaO; calculate

its percentage composition.

39. From red lead 97.65 per cent. of its weight of litharge is obtained on heating. Litharge contains 7.2 per cent. of its weight of oxygen. What are the simplest formulæ that will represent the composition of litharge and red lead?

40. Two oxides of copper are known having the formulæ Cu₂O and CuO. How would they be distinguished by name? An oxide of hydrogen is known having the formula H₂O₂; it yields oxygen on heating. How would it be distinguished by name from water?

41. What happens when quicklime is slaked with water? What evidence is there of a compound being formed? What are cons-

pounds with water termed?

42. Describe the method of determining the composition of slaked lime. Describe the construction of the dessicator, and its use. It was found that slaked lime contains 24.3 per cent. of combined water. Express its composition by a formula.

43. Are the hydrates of metallic oxides usually decomposed by heat?

What hydrates resist decomposition, even at a red heat?

44. When compounds combine, do they, like elements, combine in definite proportions? What relation does the proportion in which they unite bear to the combining weight of the elements of which they are composed? Give examples.

45. What is meant by the term "metallic hydroxide"? Ferfic hydroxide contains 52.34 per cent. of iron, 44.86 per cent. of oxygen, and 2.80 per cent. of hydrogen. Express its composition

by a formula.

46. Of the two substances one is an oxide and one a hydroxide. Identify the hydroxide. (Slaked lime and dried magnesia.)

*47. Determine (1) the free water, (2) the combined water, in the metallic hydroxide, (Calcium hydroxide, undried.)

THE NON-METALLIC ELEMENTS: SULPHUR.

48. How are non-metallic elements distinguished from metallic elements?

For what reasons is oxygen classed as a non-metal?

49. Describe the several changes that occur when sulphur is heated from the solid, through the liquid, to the gaseous state. What occurs when very hot molten sulphur is suddenly cooled, and how is the modification formed distinguished from ordinary sulphur? What do you understand by "allotropy"?

53. Describe what happens when sulphur and iron filings are heated together. State your reasons for believing that chemical combination occurs. If the product were a mere mixture, what would be its behaviour to a magnet and to a solvent such as bisulphide of carbon? What formula expresses the composition of the product?

- 51. State whether sulphur is found in the free state in nature and where. Mention some native metallic sulphides. What is meant by a "double" sulphide?
- 52. When iron is treated with dilute acid, hydrogen gas is evolved, When sulphide of iron is treated in the same way, what gas is then produced? What is the composition of this gas by weight? Express by a formula.
- 53. When organic matter containing sulphur decays, what is the product of decomposition? To what is the smell of Harrogate water due?
- 54. What is meant by saying that one element can "replace" another in a chemical compound? Give examples.
- 55. What is the product of the combustion of sulphur? Express its composition by a formula. When dissolved in water, what compound is produced?
- 56. What evidence is there that sulphurous acid becomes changed into sulphuric acid by atmospheric oxidation?
- 57. Under what conditions does sulphurous anhydride combine with oxygen to form sulphuric anhydride? Illustrate your answer by a drawing of the apparatus that may be used, and express the reaction by an equation. Explain the term "contact action."
- 58. Would you regard sulphurous acid as a "stable" or an "unstable" compound, and why?
- *59. Distinguish the metal from the metallic sulphide. (Iron and sulphide of iron.)
- *60. Identify the powders. (Sulphur and quicklime.)

SULPHURIC ACID.

- 61. In what proportion does sulphuric anhydride combine with water forming sulphuric acid? Is the oil of vitriol of commerce pure sulphuric acid?
- 62. What evidence is there that sulphuric acid itself combines with water?
 What practical use is made of this?
- 63. Describe fully the method of determining the proportions in which caustic soda and sulphuric acid react to form a neutral salt.

 What is the result obtained?
- 64. Express the neutralisation of caustic soda and sulphuric acid by an equation, and state how it was proved that water was set free in quantity corresponding with the equation.
- *65. Determine the strength of the sulphuric acid solution by means of caustic soda or caustic potash.

THE SULPHATES.

66. What are Glauber's salt, Epsom salt, gypsum, selenite, potash alum, white vitriol, green vitriol, and blue vitriol? Give a general method by which they can all be produced.

67. What is meant by the "efflorescence" of a salt, and to what is it due? At what temperature is the water of crystallisation of a salt usually given off? What is meant by an "amorphous" substance?

68. In what respect does plaster of Paris differ from gypsum? Explain its use as a plaster. When is plaster of Paris said to be "dead burnt"?

69. In order to obtain a salt in a well-crystallised state, how would you proceed? In what form does alum crystallise? Draw a perfect alum crystal.

70. Name the groups, the metals of which are attacked by dilute sulphuric acid. Give one reason why zinc and iron are more easily attacked by dilute sulphuric acid than they are by water.

71. With what metallic sulphate are the crystals of zinc sulphate isomorphous? In what other respects do the two metals resemble each other?

72. What is the action of metals upon strong sulphuric acid when heated? What is meant by an "oxidising" and a "reducing" agent? Give examples.

73. Discuss the use of the terms "sulphuric acid" and "sulphate of hydrogen," "sulphate of soda" and "sulphate of sodium." In what respects is the term "sulphate of sodium" preferable?

74. What is meant by "equilibrium" in solution. State what changes might take place when the solutions (1) of a base and a salt, (2) of an acid and a salt, and (3) of two salts, are respectively mixed together, and point out what are the circumstances under which there will be no equilibrium, but complete reaction between the mixed substances. Give examples to illustrate each of the six possible cases.

75. Describe a method for preparing oxide of magnesium from Epsom salt; also for preparing sulphurous anhydride from sulphite of sodium; also for preparing sulphate of barium and caustic soda from sulphate of sodium and baryta. Give equations. To prepare I gram of copper oxide, how much blue vitrol must be used?

*76. Which of the salts contains water of crystallisation? (Sulphate of calcium and sulphate of barium.)

*77. Identify the salts. (Sodium sulphite and ferric sulphate.)

*78. Prepare a specimen of magnesia from the Epsom salt.

*79. From the copper and sulphuric acid prepare a well-crystallised specimen of copper sulphate.

*80. Determine the water of crystallisation in the sodium sulphate, and ascribe a formula to the crystallised salt.

COMMON SALT: HYDROCHLORIC ACID.

81. What is the characteristic crystalline form of common salt? Is the pure substance deliquescent, or to what impurity is the deliquescence due?

82. Hydrochloric acid and common salt not being compounds of oxygen, give a definition of acids and salts which will include these two

compounds as well as oxygenated compounds.

83. Hydrochloric acid being volatile, use may be made of the same method for its preparation that was found to serve for the preparation of sulphurous acid gas from its compounds. Fully describe such a method of preparation, and give a drawing of the apparatus employed.

84. What are the properties of hydrochloric acid gas in respect to density, combustibility, colour, taste and smell, and solubility in water? Why is it to be expected that the gas would not support com-

bustion?

85. By what physical method may the strength of a solution of hydrochloric acid be determined?

86. How would you prove that caustic soda and hydrochloric acid react in accordance with the equation—

HCl+NaOH=NaCl+H2O?

87. In what proportion does chloride of sodium exist in sea water? To what are the deliquescent properties of sea salt due? From what elements are the bromides and iodides derived, which also exist in sea water in very minute quantities?

88. Why was chloride of potassium first called "muriate of potash"? How may it be prepared from "carnallite," the double chloride of potassium and magnesium? What is "kainite," and for what

purpose is it employed?

89. How may chlorides be distinguished from the salts of other common acids?

*90. Prepare a bottle full of hydrochloric acid gas.

*91. Volumetrically determine the strength of the hydrochloric acid solution. Confirm by its relative density.

*92. Identify the three acids. (Sulphurous, sulphuric, and hydrochloric acids.)

*93. Examine the tap water and the drainage water for chlorides and sulphates.

CHLORINE.

94. By what general method can hydrochloric acid be made to give up its chlorine? Fully explain the action of, for example, red lead upon it.

95. Give an account of the preparation of chlorine gas, and represent the

reaction by which it is formed by an equation.

96. What are the properties of chlorine in respect to colour, smell and taste, density, solubility, and combustibility? Is it a supporter of combustion to all the elements which burn in air, or only to some of them? Explain the peculiar flame observed when a lighted taper is thrust into chlorine gas.

97. Describe fully the action of sunlight upon chlorine water. Is light a force which, like heat, can overcome chemical attraction?

98. Explain why chlorine is only able to act as a bleaching agent when

water is present.

99. What is bleaching powder, how is it made, and of what does it consist? What substances can be used to liberate its chlorine when required as a bleaching agent or disinfectant?

100. What is permanganate of potash, ozone, and peroxide of hydrogen? Why should these substances act as oxidising agents? Compare their action and that of chlorine with the action of sulphurous acid as bleaching agents.

*IOI. Of the two liquids one is an oxide, the other the solution of a peroxide. Identify the peroxide by its action as an oxidising agent.

(Water and peroxide of hydrogen solution.)

NITROGEN: AMMONIA.

102. Recapitulate the properties of nitrogen gas. What purpose does it serve in the atmosphere in respect to combustion? How may nitrogen be obtained from the air? What impurity will such nitrogen contain?

103. What compound of nitrogen is produced when nitrogenous organic matter decays or is destructively distilled? In what important respect does this compound differ from the corresponding com-

pounds of chlorine and sulphur?

104. How is ammonia gas prepared? Why must quicklime, and not oil of vitriol, be employed to dry the gas?

105. Describe the properties of ammonia gas in respect to its colour, smell, density, combustibility, and solubility in water. What makes ammonia gas difficult to burn, and how could it be rendered combustible?

- 106. What is the relative density of ammonia, and how is it determined?
- 107. What is the composition of sal-ammoniac, and how may it be determined synthetically?
 - 108. What is meant by the term "ammonium," and why is it employed?
- 109. How may ammonium salts be recognised?
- *110. Prepare a bottle full of ammonia gas.
- *III. Determine the strength of the solution of ammonia.
- *112. Identify the salts. (Ammonium chloride and barium chloride.)

NITRIC ACID AND THE NITRATES.

- 113. What are saltpetre and Chili saltpetre, and how are they distinguished?
- 114. What evidence is there that nitric acid is an oxygenated acid? Give the formulæ for nitric acid and nitric anhydride.
- 115. A solution containing I gram of potash (K2O) when exactly neutralised with a solution of nitric acid and evaporated, leaves a residue weighing 2.149 grams. What formula will represent the composition of the salt? What reasons are there for supposing that sodium nitrate would have an analogous composition?
- 116. How may nitric acid be prepared? Explain the occurrence of red fumes during the process.
- 117. For what reason is nitric acid spoken of as a powerful oxidising agent? Illustrate your answer by examples.
- 118. What is an explosive? Illustrate your answer by the composition and action of gunpowder.
- 119. Fully describe the action of nitric acid upon metals. Explain the difference in the gaseous products, depending upon the strength of the acid employed; also the difference in the solid product of the action of tin from that of the action of copper on nitric acid.
- 120. Name the three gaseous oxides of nitrogen, express their composition by formulæ, and state how they may be distinguished from each other and from nitrogen.
- 121. What is nitrous acid, and how may it be produced? What is the anhydride of nitrous acid, and into what two oxides of nitrogen should this unstable anhydride be decomposed when warmed?
- 122. How may nitrogen gas be prepared from a mixture of solutions of sodium nitrite and sal-ammoniac? Explain the reaction, and state why, when once the temperature is reached at which it begins, no further heating is necessary.
- 123. What is the density of nitrogen gas compared with hydrogen as unity, and how may it be determined?

- - 124. What is the action of ferrous sulphate upon nitric acid? Describe how it may be used as a test for nitrates.
- 125. What is the action of nitric acid on indigo solution? Describe how it may be used as a test for nitrates.
- 126. What do you know about the solubility of metallic nitrates?
- *127. Distinguish the nitrite from the nitrate. (Sodium nitrite and sodium nitrate.)
- *128. Volumetrically determine the strength of the nitric acid.
- *129. Identify the gaseous oxide of nitrogen. (Nitrous oxide, nitric oxide, and nitrogen peroxide.)
- *130. Prepare a bottle full of nitrogen gas

PUTREFACTION AND NITRIFICATION.

- 131. What is meant by the terms putrefaction and nitrification? Account for the nitrate of potassium found as an efflorescence on the soil round an Indian village, the nitrate of calcium crystals on a stable wall, and the deposits of nitrate of sodium in Chili.
- 132. What is the danger in the use of water contaminated with sewage for drinking purposes? An analyst's report upon a water is given in terms of "oxygen absorbed," "albuminoid ammonia," "free ammonia," "nitrates," and "chlorine." Discuss the importance of each.
- 133. State the conditions that are necessary to promote putrefaction and nitrification. How would you apply these conditions (1) to the purification of drinking water, and (2) to the increase in fertility of the soil?
- 134. Of the nitrates or ammonium salts of the soil, which are found most abundantly in drainage waters from arable land? Under what conditions does loss of nitrate from the soil occur most freely, and how may it be prevented? Discuss the use of sulphate of ammonia instead of nitrate of soda as a manure.
- *135. Report upon the suitability of the water for drinking purposes. it almost free from organic matter, nitrates, and chlorides?

PHOSPHORUS AND PHOSPHORIC ACID.

- 136. What compound does phosphorus form with hydrogen? Mention two cases in which its production may be observed.
- 137. Is phosphorus easily oxidised? Does it oxidise at the ordinary temperature? What is meant by "phosphorescence"?

- 138. With what explosive mixture are lucifer matches tipped? How are safety matches prepared? What is "amorphous phosphorus"?
- 139. Describe the preparation of phosphoric anhydride. Why must the materials and apparatus used be perfectly dry? What happens when it is mixed with water, and what further change takes place on boiling the liquid?
- 140. Give an account of the experiments made which showed that there were three phosphates of calcium. Express their composition by formulæ, and state which of them is soluble in water. What is meant by an "acid salt." How may the three salts be distinguished by name?
- 141. Of what do bone ash, appatite, and coprolite consist? What is the action of sulphuric acid upon them, and of what does the "superphosphate of lime," thus obtained, consist? Illustrate the reaction by an equation.
- 142. What is meant by "reverted phosphate," and under what conditions does reversion take place? For what reason is the ammonium phosphate contained in Peruvian guano likely to be more easily absorbed by crops, when applied as a manure, than superphosphate of lime?
- 143. What is the source of "basic slag," and of what is it composed?
- 144. Give two methods for identifying phosphoric acid.
- *145. Find whether the phosphatic material contains soluble or insoluble phosphate, or both. (Superphosphate of lime, bone meal, or guano.)

SILICA: SAND AND CLAY.

- 146. What is silica, and how may silicon be obtained from it? Express the reaction by an equation.
- 147. What is soluble glass, and how may it be prepared? Illustrate by an equation.
- 148. What is the action of sulphuric acid upon (1) a weak and (2) a strong solution of silicate of sodium? Compare with the action of sulphuric acid upon a weak and a strong solution of sulphite of sodium.
- 149. How may silica be obtained from a solution of silicic acid? What are the properties of silica in respect to colour and its solubility in water, acids, and alkalies?
- 150. How does uncombined silica occur in nature? What is the composition of the minerals felspar, mica, china clay, asbestos, meerschaum, and steatite?

151. In what proportions does silica exist in its compounds with bases? Compare phosphoric anhydride with silica in this respect.

152. How may silicate of aluminium (clay) be artificially produced?
What is the distinctive character of the precipitate obtained, and what is the effect (1) of lime upon it, and (2) of heating it?

153. What silicates are fusible and what infusible? How may the properties of the silicates in this respect be utilised in pottery making? From what are bricks made, and how does the material used differ from that required for tile-making?

154. Of what is glass composed? What silicates render glass "soft" or fusible, and what silicates render it "hard" or infusible? To

what is the green colour of bottle glass due?

155. Of what does soil consist, and how may the proportions of gravel,

sand, and clay be determined?

156. Upon what does the wetness of a soil depend? State what is meant by the "capillarity" of a soil. By what means may the porosity of a heavy soil be increased?

*157. Examine the tap water for dissolved silicates.

CARBON: MARSH GAS.

158. How are animal and vegetable charcoal prepared, and of what do they consist? Describe the process of "charcoal burning."

159. Name the three allotropic modifications of carbon. Name three other elements already studied which exist in allotropic forms. Which modification of carbon exists in lamp-black, coke, and gas carbon, and how is each of these substances produced?

160. Upon what does the use of "bone-black" as a decoloriser depend? What is the purpose of the block of animal charcoal used in a

charcoal filter?

161. Explain the power possessed by wood charcoal of absorbing gases. Describe experiments which show its porosity and absorptive power. How does this explain the use of charcoal as a deodoriser and disinfectant? What relation exists between the condensibility of gases, their solubility, and their absorption by charcoal?

162. What is marsh gas, and how is it produced in nature? Explain the danger of "fire-damp" in coal mines. What is meant by "destructive distillation," and from what substances can impure

marsh gas be produced by this means?

*163. Determine the percentage of ash in the charcoal.

*164. Determine the percentage increase of weight of wood charcoal (previously heated to redness in a tube) on exposure to air.

*165. Identify the solids. (Powdered charcoal, black oxide of manganese, and black oxide of copper.)

THE OXIDES OF CARBON.

166. Describe the method of preparation of carbonic acid gas. Explain why carbonates are decomposed by hydrochloric acid. When chalk or marble are used, why should hydrochloric, and not sulphuric, acid be employed?

167. To what substances does carbonic acid gas act as a supporter of combustion? State whether potassium and sodium would burn in the gas if magnesium is able to do so. Represent the reaction

that would occur by an equation.

168. Describe the reaction that occurs when carbonic acid gas is passed over heated charcoal. Explain the occurrence of a blue flame over a coke fire. What is the danger in the use of slow combustion stoves? What are "producer gas" and "water gas"?

169. What are the properties of carbon monoxide? How is it distinguished in (1) properties and (2) percentage composition from

carbon dioxide?

170. Describe the use of carbon as a reducing agent of metallic oxides.

State how the reduction may be carried out on a small scale, and name some of the metals which are produced by this means on a large scale. In the case of the metallurgy of magnesium from magnesium chloride, what reducing agent is employed; and in the case of mercury, why is no reducing agent necessary?

*171. Distinguish the three gaseous compounds of carbon from each other.

(Marsh gas, carbon monoxide, and carbon dioxide.)

*172. Identify the three gases. (Oxygen, hydrogen, nitrogen, ammonia [nitrous oxide, nitric oxide, nitrogen peroxide], sulphur dioxide, sulphuretted hydrogen, chlorine, hydrochloric acid gas, marsh gas, carbon monoxide, carbonic acid gas, or air.)

*173. The oxide is believed to be either ferric oxide or an oxide of lead,
To distinguish, reduce with carbonate of sodium on charcoal by
means of a blow-pipe. Lead will give soft metallic globules,

iron a black magnetic powder.

THE CARBONATES.

174. In what proportion is lime combined with carbonic acid gas in chalk? Calculate what weight of quicklime is obtained from 100 tons of chalk, and what weight of dry slaked lime will it yield?

- 175. Mention some of the important metallic carbonates occurring in nature. In what geological forms does carbonate of calcium exist, and how is lime obtained from them on the large scale?
- 176. What is meant by dissociation? Illustrate your answer by examples, and give examples of chemical decomposition which are not cases of dissociation?
- 177. What is mortar, and why does it "set"? What are "hydraulic" cements, and what is the cause of the "setting" of these?
- 178. Express the composition of carbonate and bicarbonate of sodium by formulæ. State whether the carbonates of the alkali metals (including ammonium) are soluble in water, and whether any other metallic carbonates are soluble. State also whether the alkaline carbonates can be dissociated by heat, and whether carbonates of other classes of metals resist dissociation.
- 179. What evidence is there for the existence of carbonic acid? Has it ever been obtained in the pure state? What other unstable acids does carbonic acid resemble in composition and properties?
- 180. What would be the effect of mixing together the soluble phosphate of calcium and chalk? Illustrate by an equation.
- 181. When carbonic acid gas is passed into water containing suspended chalk, the chalk dissolves. To what is this due? What happens when the liquid is boiled or mixed with an alkali?
- 182. To what is the hardness of spring water due? Why is the hardness sometimes called "temporary," sometimes "permanent"? How may water, both temporarily and permanently hard, be softened? Illustrate by equations.
- 183. Describe the properties of carbonate of ammonium. What occurs when solutions of carbonate of ammonium and gypsum are mixed together, and when dry sulphate of ammonium and chalk are warmed together? Explain the reason of the occurrence of both reactions.
- *184. By titrating with standardised sulphuric acid, determine whether the salt is carbonate of potassium or carbonate of sodium.
- *185. Determine the percentage of carbonate in the bicarbonate by strongly heating a weighed quantity till no further loss in weight occurs.
- *186. Estimate the carbonates in the tap water by means of standardised sulphuric acid. Express the result as milligrams of calcium carbonate per liter.
- *187. Identify the salts of calcium. (Calcium sulphate, bleaching powder, calcium phosphate, calcium dihydrogen phosphate, calcium carbonate, calcium silicate, calcium choride.)

THE METALS AND THEIR SALTS.

I. Potassium and Sodium.

- 188. Mention the principal compounds of potassium and sodium occurring in nature.
- 189. Describe the principal physical and chemical properties of the two metals, pointing out how they are distinguished from other metals, and how they differ from each other.
- 190. Suggest a method for preparing the hydroxides (1) from the metals, (2) from the carbonates. Can the oxides be obtained from the hydroxides by heating?
- 191. Represent the composition of the carbonates and bicarbonates by formulæ. How may the latter be prepared from the former?

 Calculate the percentage loss in weight when the bicarbonates are heated. Name one of the principal sources of carbonate of potassium.
- 192. Mention some of the principal sources of common salt. Illustrate its crystalline form by a drawing. How may chloride of potassium be obtained from carnallite? Are the crystalline chlorides of potassium and sodium hydrated or anhydrous salts?
- 193. How may the sulphates of potassium and sodium be prepared from (1) the metals, (2) the hydroxides, (3) the carbonates, (4) the chlorides, (5) the sulphites, and (6) the nitrates? Represent each reaction by an equation. Represent the composition of Glauber's salt by a formula.
- 194. What are the principal natural sources of the nitrates of potassium and sodium? Give several methods for their artificial preparation. State the principal uses to which these two nitrates are put.
- 195. Give formulæ for the three phosphates of potassium and sodium, and state how each could be prepared.
- 196. How is soluble glass prepared, and of what does it consist? In what respect does glass containing sodium silicate differ from glass containing potassium silicate?
- 197. By what test may the salts of potassium and sodium be distinguished from each other, and from the salts of all other metals?
- 198. In respect to the solubility of their salts, how are the metals of the alkalies distinguished from the metals of all other groups?

2. Calcium.

- 199. Name the most abundant compounds of calcium occurring in nature.
- 200. How is the metal calcium distinguished in its chemical properties from the metals potassium and sodium, and magnesium and zinc?
- 201. How are the oxide and hydroxide of calcium prepared on the large

scale? Compare the solubility of the hydroxide with that of caustic soda and magnesia. What purpose does the lime serve in mortar and hydraulic cement?

- 202. Name the principal natural forms of calcium carbonate. How may the carbonate be produced by precipitation from (1) lime water and (2) chloride of calcium solution? What evidence is there of the existence of a bicarbonate of calcium? Give two methods for softening water containing the dissolved bicarbonate. by equations.
- 203. Describe a method for producing chloride of calcium. Name its characteristic property, and state for what purpose it may therefore be used.
- 204. How does sulphate of calcium occur in nature? How is plaster of Paris prepared, and what is the explanation of its use as a plaster? Compare the solubility of sulphate of calcium with that of the sulphates of sodium and magnesium. When water is permanently hard with calcium sulphate, how may it be softened? Illustrate by equations.
- 205. Name some of the natural sources of calcium phosphate. Explain the action of acids, e.g. hydrochloric, sulphuric, and phosphoric acid, upon calcium phosphate, expressing the reaction by equations. What is "superphosphate of lime"? What is the action of chalk on superphosphate?
- 206. Give some methods for the preparation of calcium silicate. Explain the solubility of freshly precipitated calcium silicate in dilute acids. Is calcium silicate a fusible salt?
- 207. Name a test by which calcium salts may be distinguished.

3. Magnesium.

208. Name the principal natural sources of magnesium, and describe the physical and chemical properties of the metal.

209. How may magnesia be prepared (1) from the metal, (2) from the carbonate, (3) from any soluble salt? Describe its properties.

210. How may magnesium carbonate be prepared?

211. What is the distinctive property of magnesium chloride?

212. Give the formula for Epsom salt, and name the salt of another metal with which it is isomorphous.

213. Name some naturally occurring silicates of magnesium.

214. By what test may soluble magnesium salts be identified?

4. Iron.

215. Name the principal ores of the metal iron.

216. How may the metal be isolated from its oxide? Give the physical

and chemical properties of iron. What is steel, and how is it tempered? In the conversion of impure iron into steel by the Bessemer process how is phosphorus eliminated?

217. How may ferrous sulphate be prepared from metallic iron? Give the formula of the crystallised salt. How may ferric sulphate be obtained from ferrous sulphate? Illustrate by equations,

218. Similarly describe how ferrous and ferric chloride may be prepared. What is the difference in colour between soluble ferrous and ferric salts?

- 219. How may ferrous and ferric oxide be respectively obtained from soluble ferrous and ferric salts? State also how ferric oxide may be prepared from (1) metallic iron, (2) ferrous oxide, and (3) ferric carbonate.
- 220. How may ferrous sulphide be prepared (1) from metallic iron and (2) from a soluble ferrous salt? Explain the action of dilute acids upon ferrous sulphide.

5. Manganese.

- 221. Name one of the principal ores of manganese.
- 222. Mention three oxides of manganese, and state whether all are basic.

 If not, state which is the basic and which the acidic oxide of the three.
- 223. Which of the oxides yield oxygen on heating, and act as oxidising agents? What is the action of each on hydrochloric acid? Illustrate by equations.
- 224. Express the composition of potassium permanganate by a formula, and state how much "available" oxygen it possesses when acting as an oxidising agent.

6. Aluminium.

- 225. How does aluminium occur in nature?
- 226. Describe the chemical and physical properties of the metal.
- 227. How does alumina occur in nature, and how can it be prepared from alum? How is alumina distinguished from the other basic oxides met with in agriculture?
- 228. Judging from the analogous production of a sulphate from a carbonate, how should it be possible to prepare aluminium sulphate from the silicate? What is alum, and how may it be prepared from aluminium sulphate? Illustrate by equations.
- 229. Name some of the principal silicates of aluminium occurring in nature. What property does this salt possess that renders it of value in pottery making? What is essentially the chemical change in the burning of bricks?

Conclusions.

- 230. State the three laws of chemical combination. Illustrate them by examples.
- 231. What is meant by an "atom," and how does the assumption of the existence of atoms help us to understand each of the three laws of chemical combination? Illustrate your answer by examples.
- 232. What is meant by a "molecule"? Calculate the molecular weights of water, sulphuric acid, and alum, assuming that the formulæ given for these compounds represents the number of atoms in each molecule.
- 233. The laws of chemical combination have been found to hold good for compounds as well as elements. How does the assumption of the existence of molecules help us to understand this? Illustrate your answer by examples.
- 234. What is the constant relation between the relative densities of gaseous compounds and their molecular weights? State the hypothesis which renders this relation intelligible. Upon what grounds do we assign the molecular formulæ H₂ and N₂ to hydrogen and nitrogen?
- 235. The molecular formula of a certain gas is C_2H_6 . What should be its relative density (H=1)?
- 236. The relative density of nitric oxide gas is 15. Is its molecular formula NO or N₂O₂?
- 237. Ozone is described as an allotropic modification of oxygen. Its relative density is 24. What is its molecular relation to oxygen gas?
- 238. What volume of hydrogen gas at o° and 760 m.m. will be produced by dissolving 6.5 grams of zinc in dilute sulphuric acid?
- 239. What volume of oxygen gas at 15° and 740 m.m. can be obtained by heating 1 gram of red oxide of mercury?
- 240. What volume of hydrogen gas at 100° will unite with 10 c.c. of oxygen gas at the same temperature, and what volume of water vapour at 100° will be produced?
- 241. When I c.c. of water at 4° C. is converted into steam at 100° C., what volume will the steam occupy under normal atmospheric pressure?
- 242. To obtain I liter of chlorine gas, at 15° and 750 m.m., from hydrochloric acid, what weight of black oxide of manganese must be employed?
- 243. What is meant by "valency"? State the valency of chlorine, nitrogen, carbon, and oxygen, illustrating your answer by the formulæ of compounds these elements form with hydrogen.

- 244. How would you deduce the valency of elements which do not unite with hydrogen? Give examples of univalent, bivalent, and trivalent metals. Name some metals which have more than one valency, as shown by the existence of two series of salts.
- 245. Give examples of univalent, bivalent, trivalent, and quadrivalent groups of elements or "radicles," and illustrate each by examples.
- 246. Write the formulæ for calcium nitrate, aluminium phosphate, ferrous carbonate, cupric silicate, and ammonium sulphite.
- 247. The properties of the elements are said to be dependent upon their atomic weights. Illustrate this by the variation in properties between the elements of (1) a group of metals and (2) a group of non-metals.
- 248. Tabulate the chlorides, hydroxides, oxides, sulphides, nitrates, sulphites, sulphates, carbonates, phosphates, and silicates of hydrogen, ammonium, potassium, sodium, calcium, magnesium, iron (ferrous and ferric), and aluminium, referred to in the foregoing studies. Use the formulæ, not the names of the compounds.
- *249. Determine the relative density of carbon monoxide (H=1), and from this calculate the molecular weight. Does it correspond with the formula CO?

PART III

XXIX. THE CARBOHYDRATES

In studying the chemistry of the principal constituents of the earth's crust, oxygen is the element to which direction is constantly directed: it is the oxides of the elements, and the compounds of these oxides with each other, which form its principal constituents; it is the properties and composition of the oxides which especially serve to differentiate the elements. In studying the chemistry of the animal and vegetable kingdoms, carbon is the element round which interest centres, and it is the compounds of carbon with hydrogen, oxygen, and nitrogen, obtained directly or indirectly from animal or vegetable products, with which Part III. of these studies will especially deal. If any dry animal or vegetable substance be heated in a test-tube the substance chars, indicating that carbon is a constituent.

With respect to the constituents of plants, there are three substances especially characteristic, viz.—(1) cellulose, the substance of which the fibre of plants mainly consists, and which constitutes the membrane of the cells; (2) starch, a granular substance produced by all green plants, and deposited in large quantities in the root, stem, or seed of certain plants; and (3) sugar, a soluble substance existing in the sap. Dry specimens of these in the water oven and then heat in test-tubes. Note that they decompose, charcoal and water being produced, showing that carbon, hydrogen, and oxygen are

constituents. Prepare a strong warm solution of cane sugar. Place it in a large beaker standing upon a plate, and pour in concentrated sulphuric acid. Note that charcoal is set free, the combined water being withdrawn by the acid. Analysis shows that each substance consists of hydrogen and oxygen, in the proportion in which they form water, combined with carbon. They are therefore termed *carbohydrates*.

Examine some starch grains under a microscope. Note the shape, the nucleus, and concentric markings. To a little starch add a drop of solution of iodine in solution of iodide of potassium. Note the deep blue coloration, due to the formation of an iodide of starch. Test for starch by this method in a sliced potato, wheat grains, a turnip, and any other vegetable substance, and note in what variable quantities the starch is present. Shake a few grains of starch with cold water in a test-tube, then boil till the starch granules, which swell and burst, have become completely mingled with the water, and a thin starch paste or mucilage has been produced. Dilute a portion of this with water, and add iodine. Note that a blue solution is formed. Heat nearly to boiling: the solution becomes colourless. Allow to cool: the colour reappears. It is clear that the blue compound of iodine and starch is an unstable compound easily dissociated by heat.

To another portion of the starch mucilage add some dilute sulphuric acid and warm gently. Observe that the starch dissolves and the liquid becomes clear. Test a few drops of the solution with iodine in another test-tube, and note that the "soluble starch" formed still gives the blue compound. Now boil the main solution for a few minutes and test a few drops again with iodine. Note that a red coloration is now produced, showing that the starch has been converted into a new substance. This new product is dextrin, or "British gum," of which in the impure state this reaction with iodine is characteristic. Continue boiling the main solution, until on again testing a few drops with iodine no coloration whatever is

produced, showing that the dextrin has in turn been converted into a new body. Now add to the boiling liquid a drop of solution of sulphate of copper, and then caustic soda or potash till alkaline. Note that instead of getting black cupric oxide as would be expected, red cuprous oxide is precipitated, showing that a reducing agent is now present. This substance, into which the dextrin has been converted, is a sugar.

The foregoing changes can be carried out by alkalies as well as by acids; by "diastase," a substance existing in the leaves and germinating seeds of plants; and by "ptyalin," a substance existing in the saliva of animals. Dry heat has a similar action, and dextrin is produced on the large scale

by merely heating starch.

The starch of commerce is prepared from cereal grains such as wheat, maize, and rice; from the stem of the sago palm; from arrowroot and from potatoes; by grinding or grating, mixing with water rendered alkaline with caustic soda, straining the mixture from fibre and other impurities, and allowing it to stand for the starch to deposit. The various starches are distinguished by the size, shape, and markings of the granules. Artichokes contain a variety of starch known as inulin. This is distinguished by giving no blue colour with iodine. It is converted into fruit sugar by boiling with dilute acid.

Procure some cotton wool (nearly pure cellulose). Note that it is unchanged by boiling with water, and that iodine has no action upon it, but that it is soluble in strong sulphuric acid forming a sulphate. To some concentrated acid in a beaker kept cool by water, add cotton wool in small quantities at a time, and stir till dissolved. Dilute this solution of sulphate of cellulose very largely with water, and boil. Test a few drops of the resulting liquid with iodine, and, after longer boiling, with sulphate of copper and then potash till alkaline. Note that at first iodine gives the brown coloration characteristic of dextrin, and that afterwards the red precipitate of cuprous oxide, characteristic of a sugar, is obtained.

The percentage composition of cellulose, starch, and dextrin, as obtained by analysis, is represented by the formula $C_6H_{10}O_5$. The molecular formula is undoubtedly a multiple of this, for the sulphate has the formula

 $C_{22}H_{14}O_4$, $_3SO_4$, and a nitrate is obtainable having the formula $C_{12}H_{14}O_4$. $_5NO_3$. The reaction by which this is produced shows that the cellulose contains hydroxyl groups like metallic hydroxides. Just as

$$\begin{aligned} & \text{KOH+HNO}_3\!=\!\text{KNO}_3\!+\!\text{H}_2\text{O},\\ &\text{so } \text{C}_{12}\text{H}_{14}\text{O}_4\text{.6NO}_3\!+\!6\text{H}_2\text{O}.\end{aligned}$$

It is obvious, therefore, that if cellulose has the formula $C_6H_{10}O_5$ it could not form a hexanitrate, for there could not be six replaceable hydroxyl groups.

The nitrate is produced by the action of a mixture of nitric and sulphuric acids on cotton wool, the object of the sulphuric acid being to combine with the water as it is liberated. If allowed to act for a short time only, the tri-, tetra-, or penta-nitrates are produced, which, when dissolved in alcohol and ether, constitute collodion. If the action is prolonged the hexanitrate—gun-cotton—is formed. Both cotton and flax consist of nearly pure cellulose. Cotton and linen rags, together with the impure cellulose constituting the fibre of straw and wood, are utilised in the manufacture of paper. For this purpose these materials are completely disintegrated and made into a pulp with water, which is then passed between rollers.

Procure some cane sugar and grape sugar. To a solution of each add copper sulphate solution and then potash till alkaline. Note that in neither case is a precipitate obtained, owing to the property that sugars possess of forming soluble compounds with many basic oxides. Now warm the solutions. Note that the cane sugar solution is unchanged, but that the grape sugar reduces the cupric to red cuprous oxide, which is precipitated. Warm another portion of the cane sugar solution with dilute sulphuric acid for a few minutes, and repeat the test. Note that the cupric oxide is now reduced to cuprous, showing that grape sugar has been formed by warming the cane sugar with acid.

"Cane sugar" occurs in unripe fruits and in the sap of plants, especially the sugar cane, sugar maple, sorghum, and sugar beet. Sugar is prepared from these. An aqueous solution is obtained, which is decolorised by animal charcoal and evaporated till crystallisation commences. Among agricultural crops, mangolds and beet are the richest in sugar. "Grape sugar" occurs, together with an equal quantity of "fruit sugar," in ripe fruits, obviously produced from the cane sugar in the unripe fruit. It is

prepared commercially by the action of dilute acid on starch. "Milk sugar" is a constituent of milk, and can be obtained by evaporating the whey of milk. On warming with acids it is converted into equal quantities of grape sugar and a sugar called "galactose." "Maltose" is the sugar first produced by the action of acid or diastase on starch; the acid, however, further converts it into grape sugar. In addition to the foregoing carbohydrates, gums belong to the same group. The "arabin" of gum-arabic has the formula $C_{12}H_{22}O_{11}$.

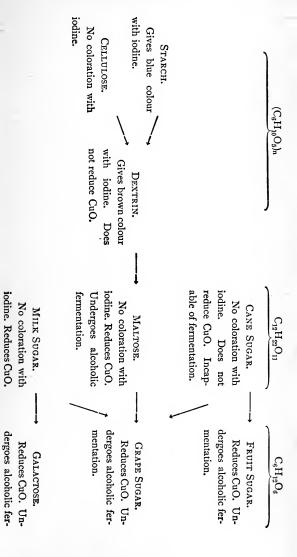
The relation of the carbohydrates to each other will be best understood by reference to the table on the opposite page. The formulæ show that the action of dilute sulphuric acid in converting starch, cellulose, and dextrin into malt sugar, and maltose, cane sugar, and milk sugar into fruit sugar, grape sugar, and galactose, is a process of *hydrolysis*, *i.e.* the decomposition of a substance by water, thus:—

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_{6}$$

XXX. THE HYDROCARBONS

THE conversion of wood into charcoal is essentially decomposition of cellulose into carbon and water. This *carbonisation* takes place in nature. Peat and lignite are partially carbonised vegetable matter, bituminous coal more completely, while anthracite consists almost entirely of carbon. The following results of analyses show the progressive carbonisation that has taken place:—

			Carbon.	Hydrogen.	Oxygen.
Wood			100	12.18	83.07
Peat			100	. 9.85	55.67
Lignite			100	8.37	42.42
Bitumine	ous c	oal	100	6.12	21.23
Anthraci	te		100	2.84	1.74



mentation.

Undergoes lactic fer-

mentation.

It was found (p. 104) that when wood is distilled inflammable gases are obtained, one of which is the hydrocarbon marsh gas. Similarly, when coal is distilled, the product is the mixture of hydrocarbons and other gases known as coal gas. When the carboniferous shale of the coal measures is distilled the chief product is a mixture of hydrocarbons called paraffin. American petroleum has a composition similar to paraffin, and is perhaps a product of the natural distillation of carbonaceous substances. It is obtained in Pennsylvania and other districts from borings through the strata overlying the sand or gravel in which the petroleum exists. Analyses and determinations of the vapour density show that both petroleum and paraffin are mixtures of hydrocarbons differing in their proportion of carbon to hydrogen and in molecular weight. Marsh gas or methane is the simplest of these hydrocarbons, and that which contains the largest proportion of hydrogen. Of the other hydrocarbons in the mixture a few are gases, but the more complex are liquids and the most complex are The relation between the physical properties and chemical composition is shown in the following table:-

GASEOUS HYDROCARBONS.			BONS.	Liquid Hydrocarbons.			
			Liquefying Point.		Boiling Point.		
Methane, CH ₄			- 164°	Pentane, C ₅ H ₁₂ .	. 38°		
Ethane, C ₂ H ₆			?	Hexane, C ₆ H ₁₄	. 71°		
Propane, C ₃ H ₈			– 17°	etc. etc.	etc.		
Butane, C ₄ H ₁₀	•		+ 1°	Pentadecane, C ₁₅ H ₃₂	. 271°		

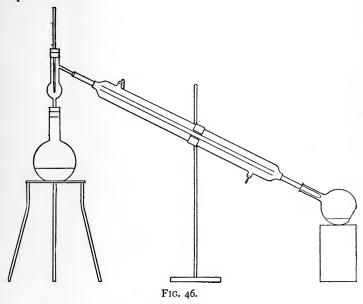
SOLID HYDROCARBONS.

			Melting Point.
Hexadecane, C	16H34		18°
Heptadecane,	$C_{17}H_{36}$	•.	23°
Octadecane, C1	$_{18}H_{38}$		28°
etc.	etc.	. 6	etc.

By fractional distillation petroleum can be separated into:-(1) A gas used for heating and lighting.

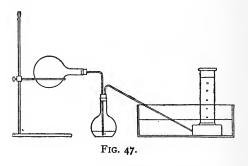
- (2) Light petroleum,—naphtha, gasoline, benzoline, benzine, kerosene,—volatile liquids used as solvents, fuels, and illuminants.
- (3) Heavy petroleum,—mineral sperm oil, etc.,—oily liquids used chiefly as lubricants.
- (4) Petroleum jelly—vaseline, etc.—used chiefly as lubricants and unguents.

Similar products are obtained from Russian petroleum and from paraffin. From the latter the product corresponding to liquid petroleum is termed paraffin oil. The solid product is paraffin wax.



Fractionate some crude petroleum by means of an apparatus such as that figured. The purpose of the tube bearing the thermometer is to allow the condensation

of the heavier hydrocarbons carried up with the vapour of the lighter hydrocarbons. Heat the flask very cautiously at first by means of a water bath, and avoid having any light near. Then, when nothing further distils, the flask may be safely heated by means of a Bunsen burner. Should, at first, some incondensible gas be obtained, collect a tube full by downward displacement; ignite it, and note that it burns with a flame much more luminous than pure marsh gas, for it contains hydrocarbons richer in carbon. As the temperature shown by the thermometer gradually rises, collect liquid fractions below 200° (light petroleum) and between 200° and 400° (heavy petroleum). Pour a few drops of each upon the hand, and note the difference in the volatility. Allow the residue to cool in the flask to obtain the semi-solid hydrocarbon residue.



To illustrate the manufacture of coal gas by the destructive distillation of coal, employ the apparatus figured. Roughly powder some coal, introduce into a Florence flask, and heat strongly. Pass the volatile products of distillation through a flask containing water in order to separate condensible products, and collect the purified coal gas in a cylinder over water. Ignite a cylinder of the gas. Note that it burns with a flame more luminous than the wood gas, indicating the

presence of hydrocarbons richer in carbon. When the distillation is completed note (1) that coke is left behind in the Florence flask, (2) that coal tar has collected in the wash flask, (3) that the aqueous liquid in the wash flask is alkaline to litmus, and has the pungent smell of ammonia. Pour off this "ammoniacal liquor" into a distillation flask, add lime, and distil off the ammonia into a little dilute sulphuric acid. Evaporate the solution in a dish to obtain crystals of sulphate of ammonium. To a portion add caustic potash solution. Note the smell of ammonia gas set free.

Coal Gas.—For the manufacture of coal gas, coal is heated in fire-clay retorts. The volatile products are passed into the "hydraulic main"—a reservoir where tar and an aqueous liquid condense. The gas now traverses "condensers,"—upright iron tubes exposed to the air, in which a further quantity of tar and water condense, and "scrubbers,"—towers in which the gas is met by a stream of water to dissolve out ammonia. The gas next passes through "purifiers," in which it is first led over hydrated ferric oxide to remove the last traces of sulphuretted hydrogen (a part having previously been removed with the ammonia), the product of combustion of which—sulphur dioxide—is injurious, and then over slaked lime to remove carbonic acid gas, which diminishes the luminosity of burning coal gas. The coal gas is finally stored in gas-holders.

With respect to its composition, coal gas may contain-

HEAT GIVERS.			LIGHT	Givei	RS.	
Hydrogen, H	•	35%	Ethylene, C ₂ H ₄ Propylene, C ₃ H ₆ Benzene, C ₆ H ₆		:	2% 1% 1%

IMPURITIES.

Nitrogen .	•	•	•	•	•	1%
Carbon dioxide						1%
Sulphuretted hyd	roge	n and	oxyg	en	•	Trace

The proportion of illuminants will depend upon (1) the kind of coal used, cannel coal yielding a much larger proportion than other bituminous coal; and (2) the temperature of distillation, a larger proportion being formed at low than at high temperatures. Gas of low illuminating power may be enriched by vapours of oils of high illuminating power.

Among the by-products of coal gas manufacture, the most important are: (1) Coke. (2) Gas carbon, formed as a deposit within the retorts, and used for the "carbons" of galvanic batteries, and the poles of the electric arc light. (3) Coal tar. From this, coal tar oil is separated by distillation, pitch being left as a residue. From the coal tar oil are obtained the hydrocarbons benzene or benzole, C₆H₆; naphthalene, C₁₀H₈; and anthracene, C14H10; from which the aniline, naphthalene, and alizarine dyes are respectively derived. (4) Ammonia in the form of sulphate. (5) Gas lime, a mixture containing chalk and unchanged slaked lime, together with the sulphide and oxysulphide of calcium in cases where the sulphur has not been removed by hydrated ferric oxide.

Hydrocarbons burn with flames which are (1) non-luminous, (2) luminous, and (3) smoky, depending upon the proportion of carbon they contain. The luminosity of flame, in fact, appears to be chiefly due to the incandescence of particles of carbon set free owing to the decomposition of the hydro-Place a clean white dish in any luminous hydrocarbon flame. Note that it becomes covered with soot. Observe that the flame essentially consists of three parts—(1) a dark interior, consisting of unburnt but decomposing gases; (2) a luminous zone, consisting of burning but incompletely burnt gases; and (3) a non-luminous envelope, in which complete combustion to carbonic acid gas and water is taking place. (This envelope may be rendered visible by volatilising



a little common salt on a piece of platinum wire in the flame.) Depress a sheet of paper into the flame of a paraffin candle. Note that a ring of charred paper is produced round an uncharred interior, showing that the flame is hollow. When air is admitted into the interior of a hydrocarbon flame, carbon is no longer set free, and the flame is thus rendered non-luminous. In the Bunsen burner (Fig. 48) air is admitted by holes at the bottom of the tube. If these be closed, the flame becomes luminous.

Fuels.-The combustibles used for heating must yield gaseous and noninjurious products of combustion. These conditions are alone fulfilled by carbon and hydrogen and their compounds. The "heat of combustion" of hydrogen is much greater than that of carbon, and the amount of heat produced by combustion of hydrocarbons will therefore vary with the proportion of hydrogen. The "pyrometric effect," that is, the highest temperature attainable by burning the fuel, will, however, largely depend upon the heat absorbed by the gaseous products, and is found to be greater for carbon than for hydrogen. The oxyhydrogen flame is intensely hot, partly because, being fed within with oxygen, combustion of the hydrogen takes place in a very small space. The Bunsen and blow-pipe flames are hot for the same reason. For furnaces where a very high temperature is required, coke or anthracite, which burn with very little flame, are employed. These relations are shown in the following table, in which the heat of combustion of a gram of substance is compared with the temperature attainable when the substance is used as fuel. A "heat unit" is the heat that would raise a gram of water 1° C.

Fuel.	Heat of Co	ombustion.	Pyrometric Effect. In Oxygen. In Air.		
Wood with 20 % water	2,800 h	eat units		_	
Dry wood	3,600	,,			
Charcoal	7,050	,,	_	_	
Pure carbon, C	8 , 080	,,	9 ⁸ 73°	2458°	
Olefiant gas, C ₂ H ₄	11,858	,,	5793°	2090°	
Marsh gas, CH ₄	13,063	,,	4800°	1945°	
Hydrogen, H	34,462	,,	3172°	1611°	

It is noticeable that water, both free and combined, diminishes heat production, because to eliminate, vaporise, and raise it in temperature, heat must be absorbed. Partly for the same reason, the heating effect produced by combustion in air is less than by combustion in oxygen, because the nitrogen of the air absorbs heat.

In the foregoing study, attention has been drawn to compounds that apparently form the starting-points of several series of hydrocarbons, the members of each of which differ from each other by CH_2 . The series of which methane (marsh gas) CH_4 , ethane $\mathrm{C}_2\mathrm{H}_6$, and propane $\mathrm{C}_3\mathrm{H}_8$, form the first members, is called the "paraffin series" of hydrocarbons; the members may be represented by the general formula $\mathrm{C}_n\mathrm{H}_{2n+2}$. Ethylene (olefiant gas) $\mathrm{C}_2\mathrm{H}_4$, and propylene $\mathrm{C}_3\mathrm{H}_6$, form the first members of a second series, the "olefines," having the general formula $\mathrm{C}_n\mathrm{H}_{2n}$. Acetylene $\mathrm{C}_2\mathrm{H}_2$, a gas of very high illuminating power, is the first member of a series $\mathrm{C}_n\mathrm{H}_{2n-2}$. The "terpenes" occurring in the oil of turpentine, obtained by distilling the resinous exudation of certain

conifers, and in most of the volatile oils of plants, are hydrocarbons having the formula $C_{10}H_{16}.\;\;$ Benzene, $C_{6}H_{6},\;$ is the first member of an important series, having the general formula $C_{n}H_{2n-6}$; while naphthalene and anthracene are the starting-points of a series of hydrocarbons containing a still larger proportion of carbon.

XXXI. THE ALCOHOLS: FERMENTATION

DISSOLVE 150 grams of sugar in a liter of water, place the solution in a flask fitted with a cork and delivery tube as figured,

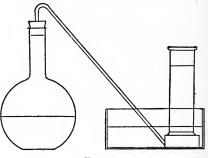


Fig. 49.

and add a few grams of yeast. Note that fermentation soon commences, and a gas is given off which, if collected in a test-tube or cylinder, will be found to extinguish a taper, and to render lime water milky. Keep the apparatus in a warm place for a few days,—a temperature of 25° to 30° C. will be found most favourable,—then, if evolution of gas has ceased, replace the delivery tube by a Liebig's condenser, and distil the mixture from a water bath, keeping the whole flask covered with a cloth to aid the process. Note that the alcohol thus obtained

has the properties of spirits of wine; for, if a glass rod be dipped in the liquid, the adhering alcohol is inflammable and burns with a pale blue flame.

In order to separate from water, distil the weak alcohol from a smaller flask. Shake the first portion of the distillate with anhydrous carbonate of potassium, a useful drying agent, then mix the alcohol with quicklime, and allow to stand for a few hours; finally distil from a flask fitted with a thermometer. Note that the nearly anhydrous alcohol begins to distil at 78° or a little over, but that the boiling point gradually rises as the distillation proceeds, this being due to other products of fermentation of higher boiling point. The alcohol may be "rectified" by fractional distillation from these impurities, which constitute, when thus separated, "fusel oil."

Yeast consists of a mass of minute organisms termed the "yeast plant," together with a chemical compound called invertase. The invertase first converts the cane sugar into grape and fruit sugar,

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

which are then converted by the yeast plant into alcohol and carbonic acid gas,

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$$

Both changes are said to be "fermentative," being brought about by organic substances of animal and vegetable origin, which remain the same before and after the reaction. The yeast plant is an "organised ferment," the invertase a "soluble ferment."

Bread.—This consists of dough which has been "raised" by aeration with carbonic acid gas and then baked. The aeration is usually effected by mixing the dough with yeast. A portion of the starch in the dough is converted into maltose, and the maltose into alcohol and carbonic acid gas, which renders the dough spongy. On baking, the air-spaces are further distended by the rise in temperature, while on the outside a crust is formed in which a part of the starch has been converted into dextrin by heat. Instead of yeast a baking powder is sometimes employed; for instance, a mixture of bicarbonate of sodium and tartaric acid, which react with each other when moistened with water, carbonic acid gas being given off and tartrate of

sodium formed. "Aerated bread" is made by mixing the flour with aerated water under pressure.

Alcohol mixes with water in all proportions. The spirit of wine of commerce is a mixture of alcohol and water. The specific gravity of pure alcohol is .795 at 15.6° C., but that of aqueous alcohol is higher, and varies with the proportion of water; so that the strength of a spirit can be found by determining the specific gravity. The strength is stated in percentage of alcohol under or over "proof spirit," *i.e.* a spirit containing 57 per cent. of alcohol by volume and having a specific gravity of .920. Rectified spirit has a specific gravity of .837, and is 56 per cent. over proof, and therefore contains 88.9 per cent. of alcohol. It can obviously be reduced to proof spirit by diluting 100 c.c. to 156 c.c. with water. Perform the experiment, using 50 c.c. of rectified spirit for the purpose. Has the product the specific gravity of proof spirit as determined by the hydrometer?

In chemical properties alcohol resembles an inorganic hydroxide, and its formula should therefore be written C_2H_5OH , hydroxide of *ethyl*, ethyl, C_2H_5 , being an "organic radicle," *i.e.* a group of elements of which carbon is one that plays the part of a single element. Thus alcohol combines with acids forming "ethereal salts,"

and when heated with a dehydrating agent loses water and is converted into the ethereal oxide "ether,"

To illustrate the formation of an ethereal salt, nitrite of ethyl or nitrous ether, the principal active constituent of sweet spirit of nitre, may be prepared. Dissolve 34.5 grams of sodium nitrite in water, dilute to 120 c.c., pour into a glass cylinder,

and cool below o° C. by surrounding the cylinder with ice sprinkled over with salt. Add 13.5 c.c. of concentrated sulphuric acid to a well-cooled mixture of 32 c.c. of rectified spirit, with an equal volume of water; dilute the mixture to 120 c.c. with water, and cool below o° C. Run the acid liquid, by means of a thistle funnel passing to the bottom of the cylinder (Fig. 40), into the nitrite solution, little by little, and constantly stirring with the thistle funnel. Note that a layer of nitrite of ethyl is formed, due to the action on the alcohol of the nitrous acid, produced from the sodium nitrite and sulphuric acid.

$$C_2H_5OH + HNO_2 = C_2H_5NO_2 + H_2O.$$

Pour off the nitrous ether into a separating funnel, shake with a little ice-cold water, run off the water, dry the ether by shaking with fused potassium carbonate, and preserve in a stoppered bottle.

Ethereal salts are more or less easily decomposed by water. Shake a little of the nitrous ether with water, and note that hydrolysis occurs, red nitrous fumes being formed.

$${\rm C_2H_5NO_2 + H_2O = C_2H_5OH + HNO_2}.$$

Decomposition generally takes place more readily in presence of an alkali. If some of the ethyl nitrite be mixed with strong alcoholic potash, and the mixture warmed in a flask fitted with an upright condenser, the ether is decomposed, nitrite of potassium being in this case produced.

$$C_2H_5NO_2 + KOH = C_2H_5OH + KNO_2.$$

Such a decomposition is termed saponification (see p. 157).

Alcohol, $\rm C_2H_5OH$, may obviously be regarded as ethane, $\rm C_2H_6$, in which hydrogen has been replaced by hydroxyl. Other hydrocarbons have alcohols corresponding to them, those derived from propane, butane, and pentane being constituents of fusel oil, and therefore products of alcoholic fermentation. The alcohol corresponding with methane is a constituent of the "wood spirit" contained in the aqueous distillate from wood (p. 104), and from which it may be obtained by distillation. The alcohol corresponding with benzene, termed phenol, or "carbolic acid," and that corresponding with toluene, termed cresol, are constituents of coal tar.

Hydrocarbon.	Alcohol.	Boiling Point.
•		66° C.
Methane, CII ₄	Methyl alcohol, CH ₃ OH	
Ethane, C_2H_6	Ethyl alcohol, C ₂ H ₅ OH	78°
Propane, C ₃ H ₈	Propyl alcohol, C ₃ H ₇ OH	97°
Butane, C ₄ H ₁₀	Butyl alcohol, C ₄ H ₉ OH	108°
Pentane, C ₅ H ₁₂	Amyl alcohol, C ₅ H ₁₁ OH	131°
Benzene, C ₆ H ₆	Phenol, C ₆ H ₅ OH	181°
Toluene, C.H.	Cresol, CrHoOH	188°

These alcohols are all *monohydric*, but, as is the case with inorganic hydroxides, *polyhydric* alcohols can exist. For instance, it was found that cellulose contained six replaceable hydroxyl groups. Glycerine is a trihydric alcohol derived from propane, having the formula C₃H₅(OH)₃, *glyceryl* trihydroxide, and it forms, when treated with nitric and sulphuric acids, a glyceryl trinitrate, or "nitroglycerine," which, when mixed with infusorial earth, constitutes the explosive dynamite.

Brewing.—Malt is prepared by steeping barley in water, then exposing the softened grain to the air till germination has taken place, in order that the soluble ferment diastase may be produced, and finally drying in kilns. The radicles or "combes" having been separated from the corn by treading and sifting, the malt is crushed and mashed with water at about 70°.C. During this process the starch is gelatinised and converted into dextrin and maltose by the diastase previously formed, and the soluble carbohydrates thus produced are extracted. The liquor or wort, when separated from the spent "brewer's grains," is next boiled with hops; then, after cooling fermented with yeast, alcohol and carbonic acid gas being formed. After sufficient fermentation has taken place, and two or three per cent. of alcohol has been produced, the yeast is skimmed off the surface, and the beer stored in casks. Wines are prepared by directly fermenting grape juice. Spirits are the products of distillation of wine and other fermented liquors.

XXXII, THE ORGANIC ACIDS

PLACE a pint of beer in a large flat-bottomed dish and leave exposed to the air for a week. Observe that the beer becomes sour in taste and acid to litmus. Vinegar has, in fact, been produced, the alcohol having been oxidised to acetic acid by atmospheric oxygen:—

$$C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$$

This oxidation is effected by a microscopic fungus,—the vinegar plant,—the germs of which exist in the air; and it is desirable to partly immerse in the beer a few beechwood shavings, upon which the fungus will develop, and which will therefore promote the chemical change.

Neutralise some vinegar with caustic soda, evaporate to a low bulk, slightly acidify with sulphuric acid and distil over the acetic acid, being careful to stop the process when charring commences. Note that this volatile organic acid has all the properties of an inorganic acid; it is sour in taste, it turns blue litmus red, and it neutralises alkalies and decomposes carbonates with the formation of salts.

Acetic acid is also obtained by the distillation of wood. If the aqueous liquid thus obtained (p. 104) be neutralised with soda, the wood spirit evaporated off and the residue distilled with sulphuric acid, impure acetic acid—"pyroligneous acid"—is obtained.

Just as acetic acid is obtained from ethyl alcohol by oxidation, so other organic acids may be produced from the alcohols with which they correspond in number of carbon atoms. Thus methyl alcohol, $\mathrm{CH_4O}$, yields formic acid, $\mathrm{CH_2O_2}$, and butyl alcohol, $\mathrm{C_4H_{10}O}$, yields butyric acid, $\mathrm{C_4H_8O_2}$. To a mixture of sulphuric acid and bichromate of potassium (a strong oxidising agent) add a few drops of butyl alcohol. Warm gently in a test-tube till action is complete, then boil and notice the cheese-like odour of the product of oxidation—butyric acid.

Oxidation of alcohols proceeds in two stages. Two atoms of hydrogen are first withdrawn, and an aldehyde (i.e. alcohol dehydrogenatum) left, and then an atom of oxygen is introduced and an acid formed. Formic aldehyde, CH₂O, intermediate between methyl alcohol and formic acid, is the useful antiseptic and preservative, the solution of which is known in commerce as "formalin." Benzoic aldehyde, C₇H₆O, constitutes the volatile oil of bitter almonds. It should be noted that oxidation does not always imply addition of oxygen to the substance. The withdrawal of hydrogen, with formation of water, is also held to be a process of oxidation. Conversely, reduction may imply either elimination of oxygen or addition of hydrogen.

By oxidising monohydric alcohols, monobasic acids, *i.e.* acids containing only one atom of hydrogen replaceable by metals, are obtained, but polyhydric alcohols can yield polybasic acids, *i.e.* acids containing two or more replaceable hydrogens. To show the basicity of the acids, it is convenient to represent them by formulæ in which the replaceable hydrogen precedes the remainder of the formula.

Formic acid, HCHO₂, occurs in ants and nettles. Acetic acid, HC2H3O2, vinegar and pyroligneous acid. Lactic acid, HC₃H₅O₃, sour milk. Butyric acid, HC₄H₇O₂, cream and butter as butyrate of glyceryl. Myristic acid, HC14H27O2, ,, cream and butter as myristate of glyceryl. palm oil and soft fats as palmitate of Palmitic acid, HC₁₆H₃₁O₂, glyceryl. Stearic acid, HC₁₈H₃₅O₂, hard fats as stearate of glyceryl. Oleic acid, HC18H33O2, olive oil and soft fats as oleate of glyceryl. Benzoic acid, HC7H5O2, gum benzoin. Salicylic acid, HC₇H₅O₃, oil of wintergreen as salicylate of methyl. sorrel as acid oxalate of potassium (salts Oxalic acid, H₂C₂O₄, of sorrel). grape juice as acid tartrate of potassium Tartaric acid, H₂C₄H₄O₆, (cream of tartar). Citric acid, H₃C₆H₅O₇, lime and lemon juice.

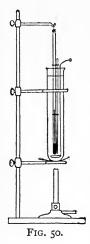
According to the formula given, oxalic acid is a di-basic acid. To confirm this, prepare a deci-normal solution, i.e. a

solution containing in one liter one-tenth of a molecular weight of crystallised oxalic acid, $H_2C_2O_4$ ·2 H_2O , in grams. Weigh out two half-gram portions of pure and previously heated sodium carbonate, dissolve each in water, and titrate with the acid, using all the precautions described on p. 71. Does the quantity of acid required correspond with that necessary to form the compound $Na_2C_2O_4$?

XXXIII. FATS AND SOAPS

ORGANIC, like inorganic, acids are able to form ethereal salts with organic hydroxides, *i.e.* alcohols. There is, for instance, the acetate of ethyl or acetic ether, C₂H₅.C₂H₃O₂, produced by distilling a mixture of alcohol, acetate of sodium, and strong sulphuric acid. The most important of these compounds are the oils or fats occurring in animal or vegetable organisms, which generally consist of *olein*, *palmitin*, and *stearin*, the oleate, palmitate, and stearate of glyceryl. Olein is an oil, while palmitin and stearin are solid fats, the latter having the higher melting point; hence hard fats largely consist of stearin, soft fats of palmitin and olein. Olive oil, sperm oil, and cod-liver oil are rich in olein, human fat and palm oil in palmitin, suet, tallow, and lard in stearin.

Just as the alcohols and hydrocarbons are distinguished from each other by their boiling points, the fats may be distinguished by their melting points. Procure some pure palmitate and pure stearate of glyceryl. Prepare a few capillary glass tubes from some odd bits of glass tubing, and seal the points. Into the fine end of one of these thrust a minute fragment of one of the pure fats, and attach the tube to a thermometer, as figured (Fig. 50) by means of india-rubber bands. Make a stirring rod



of copper wire, with the end bent into a ring of such a size that it will easily move up and down in the vessel of water without touching the thermometer and tube. Having arranged the apparatus, as figured, slowly heat the water, with constant stirring, until the fragment of fat is just melted. Note the melting point. Now allow to cool, still constantly stirring, and note the solidifying point. Repeat the alternate heating and cooling until the exact melting point and solidifying point are ascertained with certainty. Then determine the melting point of the other fat.

The melting points of the fats of special importance and their specific gravities (determined at 66° C. and compared with water at

the same temperature) are as follows:-

Fat.	Melting Point.	Specific Gravity.
Butyrin, $C_3H_5.3C_4H_7O_2$	3	1.021
Myristin, C ₃ H ₅ .3C ₁₄ H ₂₇ C	O ₂ 55° C.	5
Palmitin, C ₃ H ₅ .3C ₁₆ H ₃₁ C) ₂ 62° C.	0.900
Olein, $C_3H_5.3C_{18}H_{33}O_2$	−6° C.	0.900
Stearin, C ₃ H ₅ .3C ₁₈ H ₃₅ O ₂	72° C.	0.892

It will have been noticed that the boiling point or melting point of the hydrocarbons and alcohols of any homologous series rise as the molecular weight of the compound increases. This is obviously the case also with the fats, but with one apparent exception, viz. olein. If, however, the formulæ are examined, it will be found that whereas all the other fats are referable to the general formula, $C_3H_5.3C_nH_{2n-1}O_2$, and therefore belong to the same series, olein is not referable to this formula; so that the apparent discrepancy is understood. As a matter of fact, while butyric, myristic, palmitic, and stearic acids are derived from the paraffin series of hydrocarbons, oleic acid is derived from the olefine series. The same variation in the physical properties, with the increase in the molecular weights, is observed in the acids themselves. While formic, acetic, and butyric acids

are volatile and soluble in water, myristic, palmitic, and stearic acids are insoluble in water, and not easily volatilised; while the acids of intermediate molecular weight have intermediate properties. In fact, the boiling points are found to rise, and the solubility to diminish, as the molecular weights in a series increase.

Among the properties of fats that need to be especially noticed are (1) solubility in ether, (2) emulsification, and (3) saponification with an alkali. Bruise any dry vegetable substance, e.g. straw, maize, rice meal, linseed, or bran, in a mortar, and, having transferred to a test-tube, shake with ether. Pour off the ethereal liquid and evaporate in a dish over the water bath. The residue will consist of the fat (together with wax) of the vegetable substance.

Shake some olive oil with water; notice that the oil quickly separates from the water, and, being lighter, rises and floats upon the surface. Now add a drop of solution of caustic potash, and shake again. Observe that an emulsion is now produced, the fat being separated into minute particles which do not readily aggregate.

When fats are decomposed by saponification with an alkali, glycerine and a soap are formed. Thus:—

$$\begin{array}{lll} \textbf{C}_3\textbf{H}_5.3\textbf{C}_{18}\textbf{H}_{35}\textbf{O}_2 + 3\textbf{NaOH} = \textbf{C}_3\textbf{H}_53\textbf{OH} + 3\textbf{NaC}_{18}\textbf{H}_{35}\textbf{O}_2. \\ \textbf{Glyceryl stearate} & \textbf{Caustic} & \textbf{Glycerine.} & \textbf{Sodium stearate} \\ \textbf{or stearin.} & \textbf{soda.} & \textbf{or soap.} \end{array}$$

Boil together in an iron dish 50 grams of tallow with caustic soda, in slight excess as calculated from the equation, dissolved in 250 c.c. of water, until complete saponification has occurred. Add strong brine to the mixture to "salt out" the soap, it being insoluble in solution of common salt. Separate from the soap the aqueous liquid containing the glycerine, evaporate it to dryness, dissolve out the glycerine from the residue with strong alcohol, and evaporate the alcoholic solution until a syrupy residue of the glycerine is obtained. Note its sweet taste.

Dissolve a portion of the soap in water, place the solution in

a cylinder, and add to it dilute sulphuric acid till slightly acid Note the separation of solid stearic acid.

$$NaC_{18}H_{35}O_2 + H_2SO_4 = NaHSO_4 + HC_{18}H_{35}O_2$$
.

For preparing glycerine and the fatty acids on a large scale, fats are hydrolysed by distilling with superheated steam. The distillate consists of a solution of glycerine and a separate layer of the fatty acid. The latter is employed in the manufacture of "stearine" candles; the pure glycerine is obtained by evaporating the aqueous liquid. Fats are sometimes described as *glycerides* of the fatty acids. Thus stearin is the glyceride of stearic acid, olein the glyceride of oleic acid, etc.

It is evident that soaps are oleates, palmitates, or stearates of potassium or sodium. Potassium soaps are soft; sodium soaps are hard. When dissolved in water for washing purposes, a little hydrolysis occurs, and soda or potash is set free, which dissolves the grease from, and therefore cleanses, the hands. When used with hard water, a curd is formed owing to the formation of insoluble oleates, palmitates, and stearates of calcium and magnesium, the soaps of the alkali metals being the only soaps soluble in water. To the solution of the soap add dilute solutions of calcium and magnesium salts. Note the curdy precipitates of the calcium and magnesium salts of the fatty acids.

$$\begin{array}{l} 2 \text{NaC}_{18} \text{H}_{35} \text{O}_2 + \text{CaH}_2 \text{2CO}_3 = 2 \text{NaHCO}_3 + \text{Ca2C}_{18} \text{H}_{35} \text{O}_2 \\ 2 \text{NaC}_{18} \text{H}_{35} \text{O}_2 + \text{MgSO}_4 = \text{Na}_2 \text{SO}_4 + \text{Mg2C}_{18} \text{H}_{35} \text{O}_2. \end{array}$$

By making use of these reactions, the total, permanent and temporary hardness of tap water may be compared and approximately determined. To determine the total hardness place 70 c.c. of the water in a stoppered bottle, and run in—in very small quantities at a time, until a permanent lather is produced after shaking—a standardised solution of soap in weak alcohol (supplied), of such a strength that 1 c.c. of the solution will exactly precipitate .oo1 gram of calcium carbonate in a state of solution in 70 c.c. of water. Each c.c. of the soap solution used will then represent one "degree of hardness," i.e. one grain of

calcium carbonate in one gallon of the water (70,000 grains). To determine the permanent hardness repeat the determination with a second 70 c.c. of the water; but first boil it gently for half an hour to precipitate the carbonates of calcium and magnesium, and make up again to 70 c.c. with boiled distilled water. The number of c.cs. of soap solution now required will indicate the degrees of permanent hardness. The difference between the two results gives the temporary hardness.

Butter.—The cream that rises to the surface of milk consists of minute globules of fat. These aggregate when agitated by churning and form butter. Butter, therefore, consists chiefly of fat, but also contains 8 to 16 per cent. of water, and I to 2 per cent. of curd, with a variable quantity of added salt. The fat consists of the glycerides of oleic, palmitic, stearic, and myristic acids (the last in small quantity), together with the glycerides of certain volatile acids soluble in water, the chief of which is butyric acid. Of these combined acids the volatile acids form about 8 per cent., the oleic acid 36 per cent., and the palmitic, stearic, and myristic acids about 49.5 per cent. of the butter fat. The specific gravity of butter fat varies between .910 and .914 at 37.7° C. Animal fats used to adulterate butter, and in the manufacture of oleo-margarine, are devoid of the glycerides of the soluble acids; and the specific gravity of these being higher than that of olein, palmitin, and stearin, such fats have a lower specific gravity-...903 to .905 at 37.7° C. The purity of butter can therefore be determined by taking the specific gravity. For this purpose the butter is melted, and the liquid fat poured off from the water and curd, and filtered into the specific gravity bottle. The specific gravity is determined at 37.7° C. (100° F.). It is not always possible to detect a small amount of foreign fat in butter by this method, and in this case the purity of the butter is determined by saponifying, acidifying the soap produced, weighing the insoluble acids thrown out of solution, and titrating the aqueous liquid containing the soluble acids with a standard solution of alkali. In this way the proportion of the soluble and volatile acids to the insoluble and non-volatile acids is determined.

XXXIV. AMMONIA DERIVATIVES—ALKALOIDS AND AMIDES

In the foregoing studies it has been observed that organic compounds may be regarded as simple inorganic compounds in which an element is replaced by an organic radicle, *i.e.* a group of elements, of which carbon is one, which plays the part of an element. Thus alcohol, C_2H_5 .OH, is water, H.OH, in which hydrogen has been replaced by ethyl. Acetic acid, H.C₂H₃O₂, is hydrochloric acid, H.Cl, in which the acetic radicle has been substituted for chlorine. Similarly there is a group of organic compounds which are regarded as substituted ammonias, *i.e.* ammonia, NH₃, in which one or more atoms of hydrogen are replaced by organic radicles. These compounds are termed amines and alkaloids. They are alkaline in reaction, like ammonia, and combine with acids forming salts.

An important amine is trimethylamine, N(CH₃)₃, the substance to which the fishy smell of herring brine is due. Pyridine—NC₅H₅—is a volatile base of powerful odour produced in the distillation of coal, and usually found as the sulphate in small quantities in commercial sulphate of ammonia. Alkaloids frequently exist in plants, and to them the medicinal or toxic properties of plants are often due. Thus quinine, an alkaloid found in cinchona bark, atropine or atropia in belladonna, aconitine in aconite, morphine or morphia in opium, and nicotine in tobacco, are the active constituents of these plants.

Mix some sulphate of quinine with water in a stoppered separatory funnel. Note that this salt is almost insoluble. Now add a little dilute sulphuric acid to convert the sulphate into the soluble acid sulphate, and to the clear solution thus obtained add solution of caustic soda in order to precipitate the alkaloid itself. Shake the white mixture with ether until the alkaloid is completely dissolved in the ether, run off the water,

wash the ethereal solution by shaking with a little water, and finally pour into a dish and evaporate off the ether over warm water. Moisten the white residue with water, and test its alkalinity with red litmus paper.

These reactions show that in all chemical respects an alkaloid behaves like ammonia. The reactions may be expressed as follows. Since quinine has the complex molecular formula $C_{20}H_{24}N_2O_2$, it is symbolised in the equations by the letter A.

$$\begin{aligned} &A_2.H_2SO_4 + H_2SO_4 = 2(A.H_2SO_4)\\ like & (NH_3)_2.H_2SO_4 + H_2SO_4 = 2(NH_3.H_2SO_4) \ ;\\ &A.H_2SO_4 + 2NaOH = A + Na_2SO_4 + 2H_2O\\ like & NH_3.H_2SO_4 + 2NaOH = NH_3 + Na_2SO_4 + 2H_2O. \end{aligned}$$

The ammonia derivatives in which hydrogen has been replaced by an acid radicle are termed amides. To this group belong caffeine or theine, the stimulating constituent of tea and coffee; the theobromine of cocoa; asparagine, an abundant constituent of asparagus and many root crops; and the uric acid of urine.

Another amide is the urea or carbamide, CO(NH₂)₂, of urine. Evaporate half a liter of urine to about one quarter its bulk, and after cooling add nitric acid until crystals of the nitrate of urea begin to separate. Allow to stand, till the precipitation of crystals is complete. Filter, dissolve the crystals in a very little water, and then add strong nitric acid in which the salt is only slightly soluble. Collect the crystals which are deposited, press between filter paper to dry them, and preserve. A stable or urinal frequently smells strongly of ammonia. This is due to the hydrolysis of the urea of the urine by the action of a micro-organism, ammonia and carbonic acid gas being formed.

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3$$
.

The hydrolysis may also be effected by heating with strong caustic potash, ammonia and carbonate of potassium being

produced. Try the experiment, and observe whether ammonia is evolved.

Among other nitrogenous organic compounds should be mentioned cyanogen, CN, an organic radicle resembling in many respects chlorine. Thus it forms hydrocyanic acid (prussic acid), HCN, like hydrochloric acid, and cyanide of potassium, KCN, like chloride of potassium, etc. These cyanides have a great tendency to form double salts. Among the most important of these is ferrocyanide of potassium ("yellow prussiate of potash"), K₄Fe(CN)₆. When treated with a solution of ferric chloride, this yields ferric ferrocyanide, the well-known pigment "prussian blue." It forms, therefore, a very delicate test for iron. If the ferrocyanide of potassium be warmed with dilute sulphuric acid, hydrocyanic acid will be set free, and if smelt cautiously (it is intensely poisonous) will serve to illustrate the characteristic odour of oil of bitter almonds possessed by this acid.

XXXV. THE ALBUMINOIDS

The albuminoids, as their name implies, resemble albumin or white of egg in general properties. Their constitution is not fully known, and they possess a somewhat indefinite composition, but all contain 50 to 55% carbon, 6.9 to 7.5% hydrogen, 20 to 24% oxygen, 15 to 18% nitrogen, and (possibly with some exceptions) .3 to 2% sulphur. Dry some white of egg over a water bath, mix it with soda lime, and heat strongly in a test-tube. Note that ammonia is given off, showing that the albuminoid is a nitrogen compound. Empty the solid residue into a beaker, and add excess of dilute sulphuric acid. Note that sulphuretted hydrogen, recognised by its smell and by the black stain of sulphide of lead it produces on paper soaked in a solution of lead acetate, is evolved, showing that sulphur also is a constituent of the albuminoid.

The albuminoids have not yet been synthetically prepared in

the laboratory: they are products of vegetable life, and form an essential part of the food and of the substance of animals. Bruise some fresh clover plants in a mortar, press out the sap, filter into a test-tube, and warm. Note that a substance previously dissolved *coagulates* on warming. An albumin-like substance is thus shown to be present. Repeat the experiment with fresh meat juice. Notice here again the presence of an albuminoid.

While found in animal or vegetable substance in a soluble state, albuminoids also exist in the insoluble or coagulated state. Make some wheat flour into a dough with water, enclose in a muslin bag, and knead in a basin of water until the starch has been entirely washed out. On opening the bag, a tough elastic substance, the "gluten" of wheat, will be found, this being a mixture of albuminoids mostly insoluble in water.

The albuminoids arrange themselves in several classes distinguished by different properties. Among these distinguishing features are the different conditions under which coagulation occurs. To illustrate these, the coagulation of the albumin of egg, the casein of milk, and the fibrin of blood or myosin of flesh, may be studied.

Separate the white of a fresh egg. Shake it vigorously with about ten times its bulk of water, and strain the liquid several times through muslin until a clear solution of *albumin* is obtained. Heat a portion in a test-tube. Observe that it coagulates at a temperature below 75° C. To another portion add nitric acid, and notice that this also causes coagulation.

Allow some milk to stand for a day in a cylinder in order to allow the cream to separate. Remove some of the skim milk by means of a pipette, and heat it in a test-tube. Note that no change occurs. Now add some nitric acid, and observe the curdling of the milk due to coagulation of the casein. To another portion add rennet (i.e. the solution of a soluble ferment obtained from the fourth stomach of calves). Coagulation will again take place.

Procure some fresh blood. Notice that after a very few minutes' exposure to the air the blood spontaneously coagulates, a "clot" containing the *fibrin* being formed, while the "serum," containing blood albumin, separates. Enclose the clot in a muslin bag tied over the nozzle of a water tap, and allow water to run through, constantly kneading it with the hand meanwhile until the red colouring substance is washed away, and the fibrin is left white.

Procure some raw meat. Note that the solid matter is already insoluble and coagulated. Knead it in a muslin bag under water until colourless *myosin* is obtained.

The albuminoids are then all characterised by this property of coagulation, but while fibrin and myosin spontaneously coagulate, albumin only coagulates on heating or upon the addition of acid, and casein, which does not coagulate on heating, does so on the addition of either acid or rennet. The albuminoids are further distinguished as a class by the property of peptonisation, *i.e.* the conversion of the coagulated albuminoids into soluble compounds termed *peptones*. This chemical change may be brought about by dilute acids, but it is most easily effected by certain soluble ferments acting in some cases in acid, and in some cases in alkaline liquids.

Cut a little of the white of a boiled egg into thin strips, and mix with a solution of pepsin (a soluble ferment found in the gastric juice of the stomachs of animals) in dilute hydrochloric acid, and digest for a few hours at a temperature of 36° C. (blood heat). Note that the albumin dissolves. Boil the liquid: coagulation no longer occurs; the albuminoid has been converted into a soluble peptone.

The solutions of albuminoids and peptones are further distinguished by their behaviour on diffusion. To illustrate liquid diffusion or *osmose*, securely tie pieces of parchment paper over the mouths of two thistle funnels. Run into the one funnel a solution of magenta and into the other a solution of cochineal, and then place the inverted funnels in beakers of distilled water.

Note that the magenta soon begins to pass through the parchment into the water, but the cochineal diffuses much less readily. Now repeat the experiment with starch mucilage and solution of sugar, and after a short time test the water in each beaker by appropriate tests for starch and sugar. It will be found that, as in the previous case, it is the crystallisable substance, or crystalloid, that is readily capable of diffusion, while the non-crystallisable substance, or colloid, does not easily diffuse. Now try the experiment with a solution of albumin before and after peptonisation, testing the water for diffused substance by evaporating a portion to dryness. Note that the unchanged albumin is colloid; the peptone is crystalloid.

This process obviously provides a method of separating crystalloids from colloids in solution. The method is known as dialysis. In the foregoing experiments it will be found that liquid passes through the diaphragm in each direction; and, in the cases of difficultly diffusible substances, more liquid passes into the funnel than passes out. This gives rise to increase of volume in the funnel, and consequent increase of pressure. It is this osmotic pressure to which, in the cells of plants, is largely due the flow of sap.

Milk.—1. Composition.—A drop of milk examined under a microscope is seen to be an "emulsion," and to consist chiefly of minute globules of fat floating in an aqueous liquid. The fat has a lower specific gravity than the aqueous portion, and therefore separates as "cream" on standing, or on submitting the milk to a rotatory movement in a "separator," when the greater centrifugal force of the heavier liquid causes its separation from the fat globules. This watery liquid, or "skim milk," contains the dissolved albuminoids, and of these the casein coagulates on the addition of rennet to the milk, a curd being produced, which, when compressed into a solid mass, and then ripened by keeping, constitutes "cheese." (Cheeses contain 24 to 41 per cent. of water, 23 to 39 per cent. of fat, depending on the proportion of cream in the milk used, 27 to 32 per cent. of casein, and 0.7 to 4.4 per cent. of salt.)

The "whey" from the curd still contains the albumin of milk, and this may now be coagulated by heating. If the precipitate be filtered off, and the filtrate evaporated to a low bulk, crystals of the sugar of milk are obtained. If the mother-liquor from these crystals be evaporated to dry-

ness, and the residue ignited, an ash is left, consisting of the phosphates and chlorides of potassium, sodium, calcium, and magnesium.

2. Souring of Milk.—This is due to the action of the lactic ferment, a micro-organism which converts milk sugar into lactic acid by hydrolysis:—

$$C_{12}H_{22}O_{11} + H_2O = 4C_3H_6O_3$$

Lactic acid is able to coagulate the albuminoid of milk. Warmth aids coagulation, and in hot weather it is sometimes noticed that spontaneous coagulation occurs when only very small quantities of lactic acid have been produced. This souring of milk is prevented by cooling the milk to near the freezing point, which inhibits the action of the organisms, or by heating under pressure to 120° C., a temperature which destroys the organisms, and afterwards excluding air. The souring is also retarded (1) by heating to 56° C., a temperature which destroys some germs but does not affect the taste of the milk, (2) by cooling even a few degrees, and (3) by the use of antiseptics, such as boracic acid (H₃BO₃ or B₂O₃, 3H₂O from the non-metallic element boron), borax (Na₂B₄O₇ or 2B₂O₃.Na₂O), salicylic acid and formic aldehyde, the addition of which are, however, considered inadmissible.

3. Adulteration.—Owing to the great variability in the composition of milk due to the animal, the time of milking, the pasturage, etc., the detection of adulteration by water is a matter of some difficulty. The usual method is to determine the specific gravity at 15.5° C. by means of the hydrometer (sp. gr. = 1.028 to 1.035 for pure milk; mean, 1.032), to weigh the total solids obtained by evaporating 5 grams of milk in a weighed dish on the water bath, until the weight is constant (12 to 14.5 grams per 100 grams of pure milk; mean, 12.9); and lastly, to estimate the fat by extracting it with ether or by means of a butyrometer (2.7 to 4.3 per cent.; mean, 3.77). It has been found that there is a constant relation between the fat and the specific gravity and total solids:—

$$F = .833T - 2.22 \left(\frac{100S - 100}{S} \right)$$

in which F=the fat, T=total solids, and S=specific gravity; hence it is possible to find the amount of fat by calculation, if the specific gravity and total solids are known, or the total solids by calculation if the specific gravity and fat are known.

The Chemistry of Animal and Vegetable Life.—I. Plants.—To promote the germination of seeds, warmth, moisture, and atmospheric oxygen are necessary. The starch of the seed is converted into sugar by the diastase formed during germination, and the albuminoids are converted into peptones or amides; these substances, being soluble and dialysable, can supply the growing part of the plant with nutriment. The root penetrates the soil, and thus procures the phosphates, sulphates, and nitrates of potassium, calcium, magnesium, and iron, which the acid root sap assists in dissolving.

The stem and leaves expand into the air, where, through the agency of light, "chlorophyll" is produced, and they become green. Atmospheric carbonic acid is absorbed by the leaves, and, through the agency of the chlorophyll, in presence of sunlight and warmth, reacts with water absorbed by the roots, carbohydrate being produced and oxygen set free into the air:—

$$6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2$$

From the same materials, together with the inorganic nitrates and sulphates absorbed from the soil, albuminoid is also produced. The carbohydrate and albuminoid, being convertible into soluble substances by the soluble ferments, acids, or salts also contained in the leaves, can be conveyed by the sap to the growing part of the plant, or to the seed, stem, and root, where storage of reserve material is required, and then may be deposited in an insoluble form. Thus the complex organic constituents of plants are products of reduction from simple inorganic substances, sunlight and heat being absorbed.

2. Animals.—Animals have no power of elaborating complex organic compounds from simple inorganic substances, and their food consists therefore, directly or indirectly, of vegetable products. These foods are usually insoluble and require digestion, i.e. conversion into a form in which they can pass through the membranes of the stomach and intestines into the blood. The digestive fluids are—(1) the saliva, an alkaline fluid containing a soluble ferment, ptyalin, which converts starch into malt sugar and grape sugar; (2) the gastric juice, a fluid, acid with hydrochloric acid, containing a soluble ferment, pepsin, which converts coagulated albuminoids into peptones; (3) the bile, pancreatic juice, and intestinal juice, alkaline fluids, also containing soluble ferments, which complete the conversion of starch into sugar and albuminoids into peptones, and which also emulsify and partially saponify the fats.

The blood, into which all the digested food passes, contains a purplish red compound, hæmoglobin, which becomes oxidised in the lungs to bright red oxyhæmoglobin. This compound is capable of oxidising the carbon and hydrogen of assimilated food constituents to carbonic acid gas and water, the oxyhæmoglobin being reduced to hæmoglobin. This carbonic acid gas remains dissolved in the blood till it reaches the lungs, when it is set free and oxygen again absorbed. Thus respired air becomes rich in carbonic acid gas and deficient in oxygen (see p. 23). The water produced is excreted

by the lungs, pores of the skin, or kidneys.

The heat produced by the oxidation of the carbon and hydrogen provides the power of doing work. When more carbohydrate and fat is digested than is required for oxidation, they may be deposited as fat, and this will serve as a store of fuel, and undergo oxidation when required. Work is done through the agency of muscle, which, since it is constantly undergoing oxidation, must be constantly renewed by a fresh supply of albuminoid derived from the peptones of the digested food. When albuminoids are oxidised, in addition to carbonic acid gas and water, urea is one of the products; and this, being excreted from the blood by the kidneys, is found in urine. Thus the simple substances excreted by animals are oxidation products of complex organic compounds, heat being produced during the process.

3. Food.—The constituents of food are classified into (1) heat-producers, viz. carbohydrates, fats, and amides; (2) flesh-formers and heat-producers, viz. albuminoids; (3) inorganic salts, including especially phosphate of calcium and chloride of sodium. In addition to these, water is a necessary constituent as the food-carrier, and certain alcohols and ethereal salts in the spices, alkaloids in tea, coffee, and cocoa, and the ethyl alcohol of fermented liquors, may serve a useful purpose as stimulants.

The value of a food will depend upon (1) composition and (2) digestibility. The value of food constituents as heat-producers depends upon their heat of combustion. Thus the heat of combustion of cane sugar is 97, albumin 107, fat 229, and asparagine 49, if that of starch be taken as 100. The albuminoid ratio (i.e. the proportion of albuminoids to the equivalent in starch of the other organic constituents), required in a diet, will depend upon the kind and age of the animal and the functions it is expected to perform, and will vary from 1:2 to 1:14. Digestibility varies with the kind and condition of the food and the kind of animal, ruminating animals having a considerable power of digesting cellulose, while man has none. Cooking materially affects digestibility: for instance, baking of bread and toasting it converts a portion of the starch into dextrin, and therefore increases digestibility; but the prolonged heating of albuminoids renders them much less digestible.

XXXVI. CONCLUSIONS

The carbon compounds dealt with in the foregoing studies, of which the constitution is understood, have been regarded as inorganic hydrogen compounds, in which the hydrogen, or other element, has been replaced by an *organic radicle*; and

each class of organic compounds therefore resembles some inorganic compound, which serves as a type. Thus:—

Hydrogen, HH,	•	is a type	of a hydrocarbon, e.g. ethane, CH ₃ CH ₃ .
Water, HOH .	•	,,	alcohol, e.g. ethyl alcohol, C_2H_5OH .
Water, H ₂ O .	•	"	ether, e.g. ethyl ether, $(C_2H_5)_2O$.
Potassium chloride, KCI	•	"	ethereal salt, e.g. ethyl nitrite, $C_2H_5NO_2$.
Ferric hydroxide, Fe(OH) ₃	٠	"	polyhydric alcohol, e.g. glycerine, C ₃ H ₅ (OH) ₃ .
Hydrochloric acid, HCl	•	"	monobasic acid, e.g. acetic acid, $HC_2H_3O_2$.
Hydro-sulphuric acid, H ₂ S	•	,,	polybasic acid, e.g. oxalic acid, $\text{II}_2\text{C}_2\text{O}_4$.
Sodium chloride, NaCl	٠	**	soap, <i>e.g.</i> sodium stearate, NaC ₁₈ H ₃₅ O ₂ .
Ferric chloride, FeCl ₃	•	**	fat, e.g. stearin, $C_3H_5(C_{18}H_{35}O_2)_3$.
Ammonia, NH ₃	•	**	amine, e.g. trimethylamine, N(CH ₃) ₃ .

"In mineral chemistry the radicles are simple, in organic chemistry they are compound; therein consists the whole difference. The laws whereby the compounds are formed, and their reactions regulated, are the same in both." (Dumas.)

To understand the relation between the members of each group of organic compounds, it must be pointed out that, just as in an inorganic compound an atom of hydrogen can be replaced by, or substituted for, an atom of another monad element (e.g. H in HCl by Na in NaCl), so, in an organic compound, an atom of hydrogen can be replaced by a monad organic radicle. Thus, an atom of hydrogen in methane, CH₄, can be replaced by methyl, CH₃, forming ethane, CH₃ – CH₃ or C₂H₆. One atom of hydrogen in ethane, CH₃ – CH₂, can be replaced by methyl to form propane, CH₃ – CH₂ – CH₃ or C₂H₆. So, also, an atom of hydrogen in ethyl alcohol

 ${\rm CH_3-CH_2OH}$, can be replaced by methyl to form propyl alcohol, ${\rm CH_3-CH_2-CH_2OH}$. Thus, each member of each group will differ from the preceding member by ${\rm CH_2}$, and the difference being constant, each group can be represented by a general formula. Thus, all the paraffin hydrocarbons are found to have the composition ${\rm C_nH_{2n+2}}$, and all the corresponding alcohols the composition ${\rm C_nH_{2n+1}OH}$. It has been observed that the physical properties of each group vary with the molecular complexity; the melting points of the hydrocarbons, and the boiling points of the alcohols, rose, and the relative densities of the fats fell, with each addition of ${\rm CH_2}$ to the molecular formula.

Each class of compounds is characterised by a distinguishing group. The $-CH_3$ group of the hydrocarbons becomes $-CH_2(OH)$ in the alcohols, -CHO in the aldehydes, and -CO(OH) in the acids. The relation of methane, ethane, propane, and butane, to their corresponding alcohols, aldehydes, and acids, will be made clear by the following table:—

Hydrocarbon	Methane	Ethane	Propane	Butane
R.CH ₃	H.CH ₃	CH ₃ .CH ₃	C ₂ H ₅ .CH ₃	C ₃ H ₇ .CH ₃
Alcohol	Methyl alcohol	Ethyl alcohol	Propyl alcohol	Butyl alcoho
R.CH ₂ OH	H.CH ₂ OH	CH ₃ .CH ₂ OH	C ₂ H ₅ .CH ₂ OH	C ₃ H ₇ . CH ₂ OI
Aldehyde R.CHO	Formic alde- hyde H.CHO	Acetic alde- hyde CH ₃ .CHO	Propionic alde- hyde C ₂ H ₅ .CHO	Butyric alde hyde C ₃ H ₇ .CHO
Acid	Formic acid	Acetic acid	Propionic acid	Butyric acid
R.COOH	H.COOH	CH ₃ .COOH	C ₂ H ₅ .COOH	C ₃ H ₇ .COOH

It is these characteristic groups that give to each class of organic compounds their distinctive properties. Thus, the group CO(OH) renders a compound an acid, because it is

the hydrogen of this group that is capable of being replaced by a metal or an organic radicle, forming a salt or ethereal salt respectively. For example, acetate of sodium is CH₃.CO(ONa), and acetic ether is CH₃.CO(OC₂H₅). It follows that a dibasic acid must contain two CO(OH) groups, and a tribasic acid three. A glance at the formulæ of the organic acids given on p. 154, shows that this can be the case; indeed, oxalic acid is obviously composed of 2CO(OH). A study of all organic compounds shows how exactly are their chemical, as well as their physical properties, in accordance with their molecular constitution.

Very early in these Studies the relation was observed between heat and the force of chemical attraction. A large number of additional facts have now been deduced, which show that, when chemical combination occurs, heat, or sometimes light or electricity, are produced, and, conversely, to decompose a chemical compound, heat, or sometimes light or electricity, are required. Energy is never lost; there is a definite relation between the energy employed and the work done: the heat of combustion of two elements is a means of measuring their chemical attraction; the amount of a chemical compound decomposed by an electric current is a means of measuring the quantity of electricity used.

This conservation of energy is well illustrated in the chemical processes of the animal and vegetable worlds. The chemical changes in the leaves of plants are essentially processes of reduction, carbonic acid gas and water being used, and carbohydrates and oxygen being produced. The chemical changes in the animal are essentially processes of oxidation, carbohydrate and oxygen being used, and carbonic acid gas and water produced. The former is a heat-absorbing, the latter a heat-producing, change. The energy derived from the sun's heat and light is stored as chemical energy in the combustible constituents of food, and the oxygen set free, until, when consumed as animal food, recombination takes place, and heat

is again produced. It is the manifestations of this force of chemical attraction between elements and groups of elements with which the science of chemistry is concerned.

In the course now completed, the student has dealt with the composition of air and water, the minerals of the earth's crust, and the products of animal and vegetable life, as far as was necessary to enable him to understand the principal laws that govern the composition of matter, and the properties of the substances with which he would be most intimately connected on the farm. He has become accustomed to regard change, whether in the animal, vegetable, or mineral kingdoms. as involving chemical changes, similar in kind to the examples which have been dealt with in the laboratory; and which can be controlled and modified, provided they are understood. Not only, therefore, should the knowledge acquired enable him to understand the processes of the farm, but he should now view them from an intelligent standpoint, and hence be better prepared to attack the problems presented for solution in all agricultural pursuits.

QUESTIONS AND PROBLEMS FOR REVISION AND EXAMINATION.

THE CARBOHYDRATES.

I. What is a "carbohydrate"? Name some. How do carbohydrates behave when they are heated? Explain the action of concentrated sulphuric acid on sugar.

Name the principal sources of starch, and state how it is prepared. How may starches be distinguished from each other, and by what

chemical test can starch be identified?

3. Describe the action of dilute sulphuric acid on starch mucilage, and state what is the behaviour of the liquid at each stage to solution of iodine and to alkaline copper sulphate solution. What substances, other than sulphuric acid, are able to bring about the same series of changes?

4. Describe the method by which cellulose can be converted into sugar. Express the formation of sulphate of cellulose by an equation.

5. What are collodion and gun-cotton, and how are they produced? What purpose does the sulphuric acid serve? Explain how the existence of a hexanitrate of cellulose is evidence of the molecular formula of cellulose being a multiple of $C_6H_{10}O_5$.

6. State what happens when to solutions of cane sugar and grape sugar, solutions of sulphate of copper and then caustic alkali are added. Express the changes in the copper compounds by equations.

7. How may cane sugar be converted into grape and fruit sugar? Suggest an explanation of the occurrence of the former in unripe, and the latter in ripe fruits. Explain why this conversion is spoken of as a "hydrolytic" change.

8. Name the chief sources of cane sugar. What is milk sugar, and how is it obtained? Into what sugar is starch first converted by

hydrolysis?

 Draw up a scheme illustrating the conversion of carbohydrates of the C₆H₁₀O₅ and C₁₂H₂₂O₁₁ groups into carbohydrates of the C₆H₁₂O₆ group.

*10. Identify the carbohydrate. (Starch, inulin, dextrin, cane sugar, or

grape sugar.)

*11. Find out whether the vegetable substances contain either starch, inulin, cane sugar, or grape sugar. (Potato, turnip, mangold, artichoke, carrot, apple, barley, and malted grain.)

THE HYDROCARBONS.

12. What is meant by carbonisation? Give an account of the gradual carbonisation that goes on in nature, and give examples of artificially carbonised substances.

13. Distinguish between a hydrocarbon and a carbohydrate.

14. Give an account of the sources of petroleum and paraffin, the products of their fractional distillation, and the several uses of these.

15. In what respects do the physical properties of the hydrocarbons of

the paraffin series depend upon their composition?

16. Give a full account of the manufacture of coal gas and its purification. Of what does coal gas consist, and to what constituents are the illuminating properties chiefly due? State how the temperature of the retorts affects the quality and quantity of the gas. What are the by-products of coal gas manufacture?

17. Describe the structure of a hydrocarbon flame, and state to what the luminosity is due. Describe the principle of the Bunsen burner.

- 18. Distinguish between the quantity of heat produced by the combustion of fuels, and the temperature attained. Upon what will the latter depend? Explain why a Bunsen flame is hotter than a luminous gas flame, and why combustion in oxygen gives rise to a higher temperature than combustion in air.
- 19. How many grams of water could be raised 1° in temperature by the combustion of 1 gram of carbon and of 1 gram of hydrogen respectively. Explain why the heat of combustion of marsh gas should be greater than that of olefiant gas. Why should dry wood produce more heat when burned than wet wood, and charcoal more heat than either?
- 20. Tabulate the hydrocarbons referred to, assigning each to its proper series, and showing the simple relation that exists between the members of each series.
- *21. Prepare a pure specimen of hexane from the gasoline.
- *22. Determine the relative density of the coal gas (air=1).

THE ALCOHOLS: FERMENTATION.

- 23. Fully describe the preparation of alcohol from cane sugar by fermentation. How can the alcohol be dried and rectified?
- 24. Of what does yeast consist? Distinguish between the "organised" and the "soluble" ferment, and illustrate by equations the principal change in sugar which each brings about.
- 25. Describe the use of yeast in bread-making, and the changes that go on during the raising and baking of bread. Name two means of raising bread other than by yeast.
- 26. What is "proof spirit"? How could a spirit 56 per cent. over proof and a spirit 56 per cent. under proof be converted into proof spirit?
- 27. What is meant by an "organic radicle," and of what organic radicle is alcohol the hydroxide? In what respects does alcohol resemble in its properties an inorganic hydroxide?
- 28. Give an account of the preparation of nitrous ether.
- 29. What is the action of potash upon nitrous ether? Give examples of inorganic salts which are decomposed by the same means.
- 30. Point out the similarity in the relation of water to hydrogen with that of ethyl alcohol to ethane. What alcohols are present in fusel oil, wood spirit, and coal tar oil, and to what hydrocarbons does each "correspond"?
- 31. The physical properties of the hydrocarbons were found to vary with the molecular weights; does this also hold good for the alcohols? Give examples.

- 32. What is meant by "monohydric" and "polyhydric" alcohols. Give examples. Mention some inorganic hydroxides that resemble monohydric, dihydric, and trihydric alcohols in their composition.
- 33. In what respect is cellulose an alcohol?
- 34. What is the composition of glycerine? Show by an equation how it is converted into "nitroglycerine."
- 35. Fully describe the process of malting barley and the subsequent production of beer.
- *36. Identify the alcohol by its boiling point. (Methyl, ethyl, propyl, or amyl alcohol.)
- *37. Ascertain whether the alcohol is "rectified spirit" or absolute alcohol by the hydrometer. Reduce to proof spirit by adding the required volume of water.
- *38. Prepare a pure specimen of ethyl nitrite.

THE ORGANIC ACIDS.

- 39. To what is the souring of beer due? Describe the method for the production of acetic acid.
- 40. What is pyroligneous acid, and how is it obtained?
- 41. What is an "aldehyde," and what relation do aldehydes bear to alcohols and organic acids?
- 42. By what means can alcohols other than ethyl alcohol be converted into the corresponding acids? Give equations illustrating the oxidation of methyl, ethyl, propyl, and butyl alcohols into the corresponding formic, acetic, propionic, and butyric acids.
- 43. Give examples of monobasic, dibasic, and tribasic acids, both organic and inorganic. Point out the relation between the basicity of the acids and the number of hydroxyl groups in the corresponding alcohols.
- 44. Assign formulæ to cream of tartar (acid potassium tartrate), salts of sorrel (acid potassium oxalate), sugar of lead (acetate of lead), and verdigris (hydroxy-acetate of copper, i.e. a compound intermediate between the hydroxide and the acetate).
- Give some of the natural sources of formic, acetic, lactic, butyric, myristic, palmitic, stearic, oleic, benzoic, salicylic, oxalic, tartaric, and citric acids.
- *46. Identify the crystalline acid by a volumetric determination of the quantity of a standard solution of alkali necessary to neutralise it. (Ovalic, tartaric, or citric acid.)

FATS AND SOAPS.

47. What is meant by a "fat"? Name the three principal fats, give their composition, and mention some of their sources. What are the general properties of fat?

48. What is the relation between the molecular weights of the fats and their physical properties, including the melting points and specific gravities? Do the boiling points and solubility of the free acids also

vary with the molecular weights?

49. What is meant by "saponification"? Show by an equation how stearin is saponified by caustic soda. Describe a method for the preparation of soap, and state how the free fatty acid may be prepared from it.

50. Give two methods for the preparation of glycerine from fat.

51. State the difference between hard and soft soaps, and explain the use of soap for washing purposes.

- 52. To what is the curd produced by soap in hard water due? By means of equations express the formation of these curds both with the constituents which render water temporarily, and also those which render it permanently, hard.
- Describe how the temporary and permanent hardness of water can be determined.
- 54. What is the composition of butter, and how does it differ from all other kinds of animal fat? By what two methods may the purity of butter be ascertained?

*55. Accurately determine the melting point of the fat.

- *56. From the pure Castile soap prepare a specimen of the fatty acid of which it is a glyceride.
- *57. Determine the approximate temporary and permanent hardness of the tap water.
- *58. Is the substance butter or oleo-margarine?

Ammonia Derivatives: Alkaloids and Amides.

- 59. What is meant by a "substituted ammonia," and in what respects will such a compound resemble ammonia? Give examples.
- 60. Give examples of the alkaloids found in plants. How may the alkaloid quinine be prepared from its sulphate? Illustrate the reactions by equations.
- Name some amides, and state how the amides differ in their composition from amines.
- 62. How may urea in the form of nitrate be obtained from urine? When

urine undergoes fermentation, a smell of ammonia is noticed. Illustrate by an equation the change in the urea that then takes place.

- 63. What is cyanogen, and what element does it particularly resemble? Illustrate this resemblance by formulæ representing the composition of hydrocyanic acid and potassium cyanide. Ferrocyanide of potassium reacts with ferric chloride forming prussian blue. Represent the change by an equation.
- *64. From the quinine supplied prepare a well-crystallised specimen of the sulphate.
- *65. The commercial hydrochloric acid sometimes contains ferric chloride.

 Dilute and test for iron by the prussian blue test.

THE ALBUMINOIDS.

- 66. What is an "albuminoid"? Of what elements does it consist, and how may each of these be shown to be present?
- 67. What is meant by the "coagulation" of albuminoids? Name three methods by which albuminoids may be coagulated, and give examples of each method.
- 68. Give instances of albuminoids which exist naturally in the soluble and in the coagulated state. Describe the preparation of gluten of wheat, myosin of flesh, and fibrin of blood.
- 69. What is understood by the "peptonisation" of albuminoids, and what are the substances capable of producing it?
- 70. Of what is milk composed, and how may its constituents be separated?
- 71. To what is the souring and spontaneous curdling of milk due, and by what means may souring be retarded or prevented?
- 72. What are the three data by which the purity of milk is judged, and how are they determined?
- 73. Describe the principal chemical changes that take place in seeds during germination, and their purpose. State what compounds are absorbed by the leaves and roots of the young plant from the air and soil, what are the substances elaborated in the leaves, and what are the means employed by the plant for their production. Give an equation representing the formation of starch, and state how this substance, produced in the leaves, yet finds its way into the root or seed.
- 74. What do you understand by "osmose" and "dialysis"? Define the terms "crystalloid" and "colloid," and give examples of chemical compounds belonging to both classes. How are albuminoids altered in this respect when converted into peptones? Under what circumstances is "osmotic pressure" exhibited?

75. Describe the chemical processes by which animals digest their food. State how each constituent of the digested food is utilised, and

mention the several products of excretion.

76. Classify the constituents of food according to the purposes that each serves. Give the different heat values of the various constituents, and explain what is meant by the albuminoid ratio of a food. Upon what does the digestibility of food depend, and how does cooking affect digestibility?

*77. Is the milk free from adulteration with water?

*78. Identify the substances. (Starch, sugar, asparagine, albumin.)

CONCLUSIONS.

79. What is an "organic radicle"? Illustrate by examples the statement that "in inorganic chemistry the radicles are simple, in organic chemistry they are compound."

80. What is meant by a "type" of any class of carbon compounds? Give inorganic compounds that serve as types of hydrocarbons, alcohols, ethers, monohydric and polyhydric alcohols, monobasic and poly-

basic acids, ethereal salts, fats and amines.

81. Point out the relation between the hydrocarbons-methane, ethane, propane, and butane; the alcohols-methyl, ethyl, propyl, and butyl alcohol; the acids-formic, acetic, propionic, and butyric. Express each group by a general formula which holds good for each member. Point out how the physical properties of the members of a group vary with their molecular weights.

82. Give the radicles characteristic of each group of carbon compounds, including (1) the hydrocarbons, (2) the alcohols, (3) the aldehydes,

and (4) the acids.

83. Point out the connection between the basicity of the acids and the number of carboxyl groups contained.

84. Tabulate the carbon compounds referred to in the course, showing on the one hand the hydrocarbons from which they are derived, and on the other the type to which they correspond in composition.

85. What is meant by the "conservation of energy"? Illustrate your answer by observations made during the course of inorganic chemistry, and by the chemical changes that take place in animal and vegetable life.

86. Define the "science of chemistry."

LIST OF APPARATUS AND CHEMICALS REQUIRED BY A CLASS OF ONE DOZEN STUDENTS

A. APPARATUS.

Weights, Measures, etc.

- I balance, to weigh from .001 to 100 grams.
- ı ,, ,, .ı to 1000 ,,
- 1 box of weights, .001 to 50 grams.
- I ,, ,, I to 500 ,,
- I meter measure, graduated in tenths of an inch and millimeters.
- I decimeter cube, divided into square centimeters.
- I set glass measures, 10 c.c., 50 c.c., and 250 c.c.
- I graduated liter measure, stoppered.
- I graduated pipette, 5 c.c.
- 1 set pipettes, 10 c.c., 25 c.c., and 50 c.c.
- I dozen burettes, 60 c.c.
- 1/2 ,, graduated flasks, 1/2 liter.

Physical Apparatus.

- dozen barometer tubes.
- I ,, barometric charts.
- I Boyle tube.
- I porous cell, cylindrical.
- I each hydrometers, 700-1000, and 1000-2000.
- I sheet parchment paper.
- 1 dozen thermometers, -5° to 100° C.
- ½ ,, ,, 20° to 360° C.
- I Fahrenheit alcohol thermometer.
- I dozen glass rods for density determinations, 75 × 10 m.m., with hooks.

Hardware and Wooden Apparatus.

- I blow-pipe and bellows.
- dozen mouth blow-pipes.

I dozen wooden blocks, assorted sizes.

,, Bunsen burners, with valve.

I only , large size.

dozen roses for burners.

,, sand baths, 6 inches diameter.

1 ,, tinned iron dishes, 8 inches diameter.

½ gross each corks, 3, ½, 5, 3, 7, and I inch diameter (small end).

2 sets cork borers, I to 3.

I dozen spring clips.

1 ,, screw clips.

,, triangular files.

🗼 ,, rat-tailed files.

I copper hot-water oven and bath, $12 \times 10 \times 10$ inches, on stand.

I dozen retort stands with three rings, 18 inches high,

I large retort stand with rings and three clamps.

dozen deflagrating spoons.

I iron spoon.

I dozen crucible tongs.

I ,, wire tripods.

1/2 ,, pipe-clay triangles.

,, steel watch springs.

I square foot wire gauze.

I dozen burette stands.

,, test-tube stands, 6 holes.

Porcelain and Earthenware Apparatus.

1 dozen capsules, 21 inches diameter.

I ,, crucibles with lids, 13 inches diameter.

1 ,, each basins, 3 inches and 4 inches diameter.

1 ,, mortars and pestles, 41 inches diameter.

 $\frac{1}{2}$,, soup plates.

I ,, pneumatic troughs, 12 inches, with small beehives, 1½ inches high.

Glass Apparatus (Light).

I dozen each beakers, 4 oz. and 12 oz.

I ,, ,, flasks, 4 oz., 16 oz., and 40 oz.

1 ,, wide-mouthed flasks, 2 oz.

2 ,, Florence flasks, 6 oz.

i ,, filter funnels, 3 inches.

I filter funnel, 6 inches.

I dozen thistle funnels, plain, 12 inches.

I dozen thistle funnels, safety, 12 inches.

,, retorts, stoppered, 10 oz.

,, calcium chloride tubes, 7 inches.

,, fractionation tubes, I bulb.

I gross test-tubes, 5 by § inches.

I dozen each test-tubes, 7 by 3 and 7 by 11 inches.

3 ,, U tubes, with connecting tubes attached, 4 inches.

2 ,, watch glasses, 2 inches.

Glass Apparatus (Heavy).

dozen stoppered bell jars, 9 by 5 inches.

I ,, narrow-mouth bottles, 150 c.c.

1 ,, ,, wide-mouth ,, ,,

I aspirating bottle, I gallon.

dozen lamp glasses.

,, Liebig's condensers, 14 inches.

I dessicator, including bell jar, 11 inches diameter, ground glass plate, porcelain dish, and perforated zinc plate.

I stoppered separating funnel, 150 c.c.

I dozen wide-mouth bottles, with ground tops, 40 oz.

1 ,, narrow-mouth bottles, 32 oz., fitted with cork and tubes, as

1 ,, ground glass plates, 3 inches.

1 ,, cylinders, with ground tops, 10 by 1½ inches.

I only ,, ,, I5 by 2 ,

Tubing.

10 lbs. glass tubing, 3 to 5 m.m. bore.

I lb. soft glass tubing, 15 m.m. ,,

7 lbs. combustion tubing, 12 m.m. bore.

6 feet india-rubber tubing, \frac{1}{8} in.

30 ,, ,, ,, \(\frac{1}{4}\) in. ,,

I foot thermometer tubing, cylindrical bore.

B. CHEMICALS.

All the following Chemicals to be of commercial quality unless otherwise stated.

1 lb. acetic acid, glacial.

2 lbs. alcohol (rectified spirit).

lb. fusel oil.

I oz. aluminium foil.

I ,, alumina.emery (specimen).

I lb. potash alum. kaolin (specimen). mica (specimen). felspar (specimen).

2 lbs. solution of ammonia, conc.

I lb. ammonium carbonate.

4 lbs. sal-ammoniac.

½ lb. ammonium molybdate solution.

1, ammonium oxalate.

I,, sulphate.

I oz. arsenious oxide. asparagine (specimen).

I ,, asbestos, coarse fibre.

1, platinised asbestos.

I ,, butyric acid.

1 lb. barium chloride.

1, baryta.

heavy spar (specimen). caffeine (specimen).

I grain calcium.

4 lbs. quicklime.

I lb. calcium chloride, gran.

I ,, calcium carbonate.

7 lbs. marble.

calc spar (specimen). chalk (specimen).

I lb. calcium sulphate, pure. selenite (specimen).

1, calcium phosphate.

apatite (specimen).
basic slag (specimen).
superphosphate of lime (speci-

Peruvian guano (specimen). coprolite (specimen).

bone meal (specimen).

 wood charcoal. gas carbon (specimen). lamp-black (specimen). graphite (specimen).

1 ,, chloroform, methylated.

I oz. cobalt chloride solution.

I ,, cochineal solution.

1 lb. cotton wool.

I ,, copper turnings.

4 ,, fine copper wire. brass (specimen).

,, cupric oxide, gran.

,, copper sulphate.

1, citric acid.

1,, dextrin.

1, ether, methylated.

I ,, glycerine.

½ doz. gold leaves.

½ lb. hydrogen peroxide, 5 vol.

1 w. qt. hydrochloric acid, coml.

2 lbs. hydrochloric acid, pure.

1 lb. iodine in potassium iodide solution.

iron plate (specimen). steel plate (specimen).

I ,, iron filings.

1,, ferric oxide.

1,, ferrous sulphate.

4 ,, ,, sulphide. hæmatite (specimen). iron pyrites (specimen).

½ lb. indigo solution. lead plate (specimen).

1 ,, litharge.

2 lbs. red lead.

I oz. lead acetate.
I lb. litmus solution.

I dozen books litmus paper, red and blue.

I oz. lactic acid.

I,, magenta.

1 ,, magnesium ribbon.

d lb. ,, sulphate.

I oz. magnesia. dolomite (specimen). magnesian limestone (specimen).

I lb. sodium.

chloride, pure.

steatite (specimen). 4 lbs. manganese dioxide. 14 ,, mercury. b lb. mercuric oxide. I w. qt. nitric acid, coml. I bottle compressed oxygen. 🖟 lb. oxalic acid. I oz. oleic acid. I ,, triolein. 2 feet platinum wire. I oz. palmitic acid. 1 ,, tripalmitin. I qt. crude petroleum. 1 lb. petroleum spirit. 1, paraffin wax. I oz. phosphorus. 1, amorphous phosphorus. 1 ,, phosphoric acid. $\frac{1}{2}$,, pepsin. I ,, potassium. I lb. caustic potash, sticks. I, potassium carbonate, fused. nitrate. bichromate. 1,, ,, permanganate. ,, 1,, ferrocyanide. ,, cyanide. I OZ. ,, kainite (specimen). 1,, quinine.

1 ,, silica.

4 lbs. silver sand.

I oz. salicylic acid.

flint (specimen). quartz, crystal (specimen). 10 lbs. common salt. ½ lb. sodium carbonate, pure. bicarbonate. I ., caustic soda, sticks. 2 lbs. caustic soda, powder. 🚽 lb. sodium sulphate. sulphite. nitrate. nitrite. ,, silicate. ,, I ,, soda lime. standard soap solution. starch. grape sugar. milk sugar. 4,, inulin. 4 lbs. cane sugar, lump. I lb. sulphur, roll. I w. qt. sulphuric acid, coml. 4 lbs. sulphuric acid, pure. 1 lb. liquefied sulphur dioxide I oz. stearic acid. 1 ,, tristearin. 1 lb. tin, gran. solder (specimen). I lb. tartaric acid. I oz. urea. I carboy distilled water. I lb. zinc, gran. I oz. zinc foil. 1 lb. zinc sulphate. 1 oz. zinc oxide.

The cost of the foregoing set of apparatus and chemicals, as estimated by Messrs. Baird & Tatlock, is £45 12s., net.



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When the reference to a metallic salt is required, turn to the particular salt and particular metal; the pages common to each will contain the reference.

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