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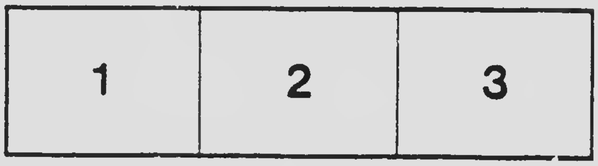

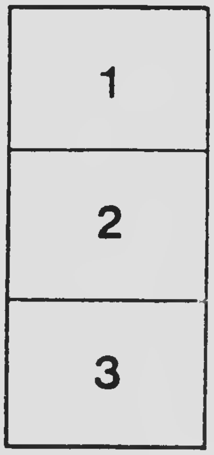

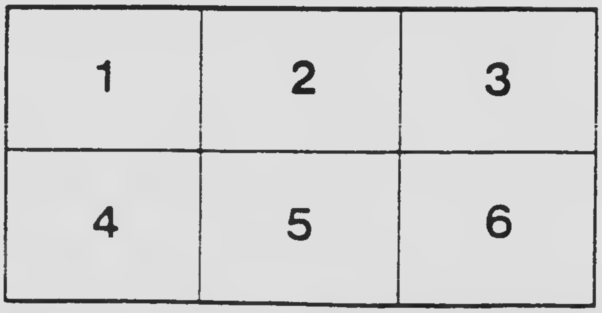

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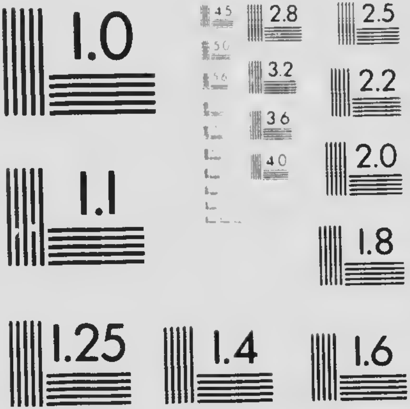
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ELEMENTARY CHEMISTRY

FOR

HIGH SCHOOLS

BY

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Authorized for use in the Schools of Quebec.
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PREFACE

No special originality is claimed for this book. Certain standard methods and illustrations in the elementary teaching of chemistry have proved themselves of such excellence that novelty in these matters generally means loss of real value. There is, however, great need of emphasis in proper places: beginners are very liable to overlook some things that are of prime importance and misunderstand others; hence, a very special effort has been made to guard against those omissions and misconceptions that are so often apparent in the case of young students.

The successful study of chemistry necessarily presupposes some knowledge of physics; but, in an elementary work like this, the quantity is very small. Acquaintance with the metric system is taken for granted, and the centigrade thermometer-scale is used throughout the book.

Science is largely a matter of observation and classification. Hence, pupils should be trained in both. Observations and experiments may be divided into three classes: those that can be carried out successfully by pupils themselves; those that can be carried out by the teacher; and those that can be carried out successfully only on the large scale or in very specially equipped laboratories. Experiments of the first class are described in detail in the following chapters, whilst others are referred to only in [illegible] way. For details concerning the performance of class-room experiments by the teacher, some such book as Newth's "Chemical Lecture Experiments" (Longman's) should be consulted. Particular attention should be paid to the recording of the results of observations; and, in this connection, the great importance of the making of sketches cannot be too strongly emphasized; attempting to describe experiments without sketches of the apparatus employed is almost like trying to prove propositions in geometry without figures. The sketches in the book have all been made in outline so as to assist the pupil in making his own.

But chemistry is much more than the making and recording of experiments; it has a most important philosophical side. Observation must be followed by classification, and this involves that all-important principle of comparison. Hence, as the study proceeds there should be constant reference to what has gone before and likenesses and unlikenesses carefully noted. Isolated facts are not science. Moreover, it is not possible to grasp the full import of many things when first met with; their meanings will develop with our own mental advance; hence, the need for frequent re-reading of chapters that go before what at the moment one may happen to be studying. The listing and tabulating of information is a most valuable exercise, as it presents in a striking way many things that might otherwise be overlooked.

What might be called the human side of the subject has not been disregarded. No one needs to remember who discovered each element or compound, or the dates of all the important happenings. But there should be in the mind of each pupil some sort of chronological perspective and an appreciation of the fact that this science is intimately connected with the history of the race and is a part of universal evolution.

It may be well to defer the study of Chapter XV, on Organic Chemistry, till all the inorganic has been gone over; but it was thought best to place it where it appears in the book in order to minimise the old and persistent idea that there is some real and fundamental difference between these two great branches of chemistry.

Certain matters which are perhaps somewhat too advanced, or not of sufficient importance, for treatment in schools, but which explain or round out that which is taught, have been introduced in small type. These little paragraphs will elucidate some things that might otherwise be obscure and may, perhaps, help in cultivating a desire for more advanced study.

While simple language has always been the writer's aim, he does not think that the vocabulary of the High School pupil should be considered as hardly more advanced than that of the infant class;

a certain number of new words, exclusive of purely technical terms, should be learned from the reading of any book. Special attention should be given to the spelling of chemical names and other terms.

Among the questions given at the end of each chapter, such as are perfectly obvious will not be found, and a few are included that might not be regarded as quite fair in an examination—the main object is to stimulate observation and cultivate thought.

Finally, the author [illegible] to place on record his sincere appreciation of the hel[illegible]ticism of Dr. R. F. Ruttan, Director of the Department of Chemistry, and that of other friends who are teachers; and to express the hope that those who use the book will write him in regard to any points which are obscure or inaccurate. He will be only too glad to reply to any such communications.

McGill University,
Montreal.

N. N. E.

CONTENTS

CHAPTER PAGE

I. INTRODUCTORY 9

II. HISTORY OF CHEMISTRY—COMBUSTION . . . 15

III. OXYGEN—OZONE 26

IV. HYDROGEN 37

V. THE GAS LAWS AND THE MOLECULAR THEORY . 44

VI. COMPOUNDS OF HYDROGEN AND OXYGEN. WATER. HYDROGEN PEROXIDE 55

VII. LAWS OF COMBINING PROPORTIONS AND THE ATOMIC THEORY 68

VIII. SYMBOLS, FORMULAS, EQUATIONS, CALCULATIONS . 76

IX. CHLORINE AND ITS COMPOUNDS—BROMINE, IODINE. FLUORINE 85

X. ACIDS. BASES. SALTS. NEUTRALISATION. ELECTROLYTIC DISSOCIATION 103

XI. SULPHUR AND ITS COMPOUNDS 109

XII. NITROGEN. THE ATMOSPHERE. COMPOUNDS OF NITROGEN 124

XIII. PHOSPHORUS. ARSENIC. ANTIMONY. BISMUTH . 142

XIV. CARBON. OXIDES OF CARBON. CARBON DISULPHIDE. CARBIDES 150

XV. OTHER COMPOUNDS OF CARBON. ORGANIC CHEMISTRY 161

XVI. SILICON. BORON 187

XVII. THE METALS 190

XVIII. THE METALS OF THE ALKALIS. SODIUM, POTASSIUM 194

XIX. THE METALS OF THE ALKALINE EARTHS. CALCIUM. MAGNESIUM 207

XX. IRON. NICKEL. COBALT 220

XXI. SILVER. COPPER. MERCURY 227

XXII. ZINC. ALUMINIUM. TIN. LEAD 236

XXIII. GOLD. PLATINUM 245

INDEX 251

TABLE OF ELEMENTS 263

ELEMENTARY CHEMISTRY

CHAPTER I

INTRODUCTORY

KNOWLEDGE. SCIENCE. THE SCIENCES. PHYSICS. CHEMISTRY.

What is Chemistry? Why should we study it? These two questions naturally arise in the minds of those who are just beginning the study of this subject, and a sort of half answer will be given in this chapter; a more satisfactory explanation will slowly grow as we get to know more and more about the subject.

Whenever we have a very large number of different objects, it is necessary that they should be arranged according to some definite system if they are to be of use; and the larger the number, the more indispensable the system becomes. A few books may be kept in almost any order on a shelf; but, in a large library—say of 100,000 volumes—unless classification is strictly followed, it is impossible to find some particular volume when wanted, and the library thus becomes more or less useless.

Exactly the same thing is true of what we have in our minds—our ideas. In the infancy of the race when ideas were few, when knowledge was very limited, arrangement was not very necessary; but to-day, when the sum of all human knowledge is vast beyond the imagination of any one individual, classification and arrangement become absolutely essential. Knowledge, then, must be carefully arranged and classified if it is to be of the highest value. Many different systems have been tried and abandoned in favor of better ones; and, to-day, knowledge arranged and classified according to the best principles that have yet been discovered, is what we call science. The distinguishing quality of science, then, is order; it differs from mere knowledge in much the same way that a regiment differs from a crowd, or a dissected picture, when the parts are properly fitted together, from the same picture when its parts are piled up pell-mell.

In principle, all knowledge may be organized into one enormous whole—which is science in its broadest and most inclusive sense. This science, however, would be so very vast that no one could possibly master it; and, hence, this total science has been subdivided, for purposes of convenience, into many sections, each called a science, and dealing with a certain distinct portion of human knowledge. One of the simplest and most useful of these subdivisions is the following:

Mathematics
Physics
Chemistry
Biology
Psychology
Sociology

Mathematics is the science of quantities; physics and chemistry we shall examine more carefully a little later on; biology, including botany and zoology, is the science of living things, plants and animals; psychology is the study of the mind and the processes and laws of thought; while sociology, the most intricate of all the sciences, is the study of social relations.

Here we have the sections arranged in their logical order, any one of them requiring a certain knowledge of those going before for its mastery. Thus, one may study mathematics successfully without knowing anything about physics;

but cannot study physics successfully without some knowledge of mathematics; and for a successful understanding of chemistry we must know something of physics, and so on. It must, of course, be remembered that this division is purely one of convenience, and the different sciences mentioned above are often found to overlap and run into one another. Thus, there are many parts of physics that cannot be properly understood without some knowledge of chemistry.

If, in working at a science, we are concerned simply in building up a knowledge as complete and accurate as possible of the facts and principles concerned, without any regard to their application to useful ends, we produce what is called a pure science. If, on the other hand, our object is to discover and classify facts and principles in order to apply them to certain useful ends, then we are working at an applied or practical science. (Pure science may be regarded as water pumped into a reservoir, capable of doing useful work if properly applied, and the cultivation of pure science is like pumping more water into this reservoir for future use; while applied science may be regarded as some of this water actually running over a water-wheel and thus driving machinery.) Chemistry may be studied both as a pure and as an applied science.

In studying certain classes of actual phenomena, we often draw on several sciences, the result being sometimes called a mixed science, which, in its turn, may be either pure or applied. Thus geology is a mixed science, certain portions of physics, chemistry and biology being employed to explain or account for the structure of the earth as we know it to-day. If the object of the study be merely to do this as completely as possible, the result is a pure (mixed) science; if, on the other hand, the intention is to use the facts and principles thus arrived at for certain useful ends, as the location of coal deposits, the tracing of metalliferous veins, &c., then we have an applied (mixed) science. Similar remarks apply to medicine and many other branches of learning.

When we look around us attentively, *i.e.*, observe, we find the space about us filled with a great many different kinds of solids, liquids and gases, which we call collectively, matter. Further, we notice that this matter is continually undergoing change. All the matter in this world, for instance, is moving—it is undergoing change in position as it whirls round the axis of the earth and also round the sun. It also undergoes changes in temperature, being sometimes warmer and sometimes cooler. Then, we notice other kinds of changes, such as the burning of wood, the rusting of iron, and the change which food undergoes in being built up into the bodies of living plants and animals. Indeed, we know of no matter that is not undergoing change of some sort or other. Now, in accordance with the "scientific method," we must observe and record all the different kinds of changes that we possibly can and then classify them somehow or other. A great many different classifications have been tried, but the one that, up to the present time, has been found most useful, starts by dividing all changes that matter undergoes into two great classes, *i.e.*, those in which the matter itself remains the same matter during the changes, and those in which the matter itself is altered. Thus, if we move a piece of wood from one place to another, the matter of the wood remains the same, the position only being altered. If we warm or cool the wood slightly, the matter still remains unchanged, as it does if we cut the wood up into tiny pieces. If, on the other hand, we heat the wood very highly, or burn it, then we do not have wood left after the change ; the matter itself has been altered and converted into something quite different to what it was before. Changes of the first kind form the subject matter of physics, those of the second kind, of chemistry.

We have, therefore, the following definitions :

Matter *is that which occupies space*, i.e., takes up room. *It possesses weight.*

Physical Changes *are those in which the composition of the matter concerned is not altered.*

Chemical Changes *are those in which the composition of the matter concerned is altered.*

Chemistry *is the science which deals with matter and those changes which it undergoes involving alteration in composition.* It is sometimes called the science of the composition of things.

In connection with definitions, it should be understood that the actual form of words used is not so very important, provided that the definition is definite, *i.e.*, contains all that it should and nothing that it should not, expressed in such a way as to allow of no misconception. The pupil, in testing a definition, and after seeing that it is complete, should ask himself, not "can this be understood," but "can this be misunderstood," and then act accordingly.

While it is generally very easy to say to which class a certain change belongs, *i.e.*, to say whether an alteration in composition has taken place or not, there are cases in which it is difficult—indeed scientific men are still very doubtful as to how they should be classified. For instance, the changes of water into steam and steam into water; or the changes of water into ice and *vice versa*, are generally called physical changes, as is also the dissolving of sugar or salt in water, and so on. But many of the leading chemists to-day think that these should be classed rather as chemical than physical changes. However, we may remember that they are still generally spoken of as physical and, until we have a good deal more knowledge of them, we cannot decide definitely.

We now have a preliminary idea as to what chemistry is. An answer to the second question asked at the beginning of this chapter, *i.e.*, why should it be studied, has only been hinted at, but will become clearer as we go on. Let us keep in mind, however, that the study of any subject is valuable in two distinct ways: first, for the actual facts and methods which it teaches us; and, secondly, for the mental gymnastics —the training of the mind—which it provides. How much of this latter good we get depends mainly on ourselves. Just as in ordinary gymnastics, it is necessary to exercise all parts of the body in proper proportion, even if what we desire is special strength in one part; so, in our study, we should exercise all our mental faculties and not, as is often the case, train our memories at the expense of our reason. It is an excellent thing to remember: it is a more excellent thing to understand.

QUESTIONS

1. To what class of changes does each of the following belong, and why? (*a*) the converting of logs into boards, (*b*) the burning of wood, (*c*) the cooking of meat, (*d*) the grinding of a scythe?

2. What are the principal pure sciences? Briefly characterise each.

3. Define the terms: matter, physical change, chemical change, chemistry.

4. Classify the following changes: (1) Fresh warm milk is (*a*) cooled; (*b*) it is then shipped to the city; but, during the journey (*c*), it turns sour. (2) A piece of steel (*a*) is magnetised; (*b*) some of it is then filed into a fine powder which (*c*) is placed in a glass of water, and (*d*) rusts.

5. How are we to distinguish whether a certain change is physical or chemical? When the answer has been written, see whether it is possible to misunderstand it.

6. Distinguish between science and knowledge.

7. Mention two reasons for studying chemistry.

8. Are chemical changes always accompanied by physical changes? Are physical by chemical?

9. Give some examples of the value of classification in connection with the ordinary activities of life.

10. Mention three physical and two chemical changes that you noticed before arriving at school this morning.

CHAPTER II

HISTORY OF CHEMISTRY — COMBUSTION

ELEMENTS. COMPOUNDS. ANALYSIS. SYNTHESIS.

As we saw in Chapter I, Chemistry is the science that makes a study of the composition of bodies and the changes in composition which these bodies undergo. We shall learn that it is a very large science. Now all the classified knowledge that we have to do with under this head did not suddenly come into existence ready arranged: men have been collecting the facts, little by little, for thousands of years, often accidentally, sometimes intentionally, and carefully comparing them; and many different classifications of these facts have been tried—much as the objects in a great museum are slowly collected and then arranged and rearranged as the collection grows. The story of how all this happened is the history of chemistry. It is a long story—far too long to be told here; but some of it is so interesting that we must briefly refer to it.

The history of chemistry is generally divided into the following periods:

The Ancient period	— 300, A.D.
The Alchemistic period	300 — 1550, "
The Iatro-chemical period	1550 — 1650, "
The Phlogistic period	1650 — 1775, "
The Quantitative, or modern period . .	1775 — "

Long, long ago, people began to take an interest in those changes that to-day we call chemical. From the very birth of the race, fire seems to have had a fascination for human beings; the souring of milk and the fermentation of sweet juices were also known, as were changes brought about in baking clay, in burning lime, in cooking meat, in tanning hides, in working metals, and so on. The Egyptian priests made large numbers of experiments, and many chemical matters are touched upon in our own Bible. But for a very long time all these things were known merely as disconnected facts—they were not classified and no relationships were studied out, so they did not form a science.

But, by degrees, certain men began to make a special study of the metals, having a belief that it was possible to convert the ordinary, or as they called them, "base" metals (*i.e.*, those that were altered in the fire) into gold and silver, the "noble" metals (those that fire did not affect). Such a change would not only be interesting in itself, but would make the man that knew how to bring it about enormously rich—and men have always had a strong desire to be rich! The men who believed that such a change could be brought about, and who made experiments with this object in view, were called alchemists, and the change of one metal into another, which they hoped to effect, was called transmutation. Many of these alchemists were exceedingly hard-working men, and performed an enormous number of experiments; and, although they never succeeded in making gold from anything else, they did discover a large number of useful and interesting substances and processes.

The alchemists thought that transmutation was to be brought about by a wonderful substance called the "philosopher's stone," a minute quantity of which was capable of changing a very large quantity of base metal into gold or silver. They also believed in the possibility of preparing a marvellous medicine, called the "elixir of life," which would cure all diseases and endow those who employed it with perpetual youth. A third thing that many of them tried to prepare was the "universal solvent," a potent liquid capable of dissolving everything: just what this liquid, when discovered, was to be kept in they do not seem to have worried about! Many of the alchemists were perfectly sincere in their work, but many others were dishonest—mere charlatans—who pretended to have discovered the secret of transmutation, and sold their worthless receipts for large sums of money to those who were silly enough to buy them, and then disappeared.

Alchemistic beliefs, or pretended beliefs, have persisted to a certain extent almost to the present day. About the year 1885, a man turned up in Montreal who professed to be in possession of a method for converting lead into gold by means of a secret powder, and he gave a demonstration of his process to which he admitted a few favored gentlemen on payment of a small fee; but he did not succeed in interesting these capitalists any further, and he disappeared, leaving behind the small piece of real gold which he professed to have produced from lead.

Gradually, however, as years passed and failure followed failure, belief in the possibility of transmutation became less and less and the workers turned their attention to other things. In particular, chemistry was looked on more and more as a valuable aid to medical men in the preparation of substances used as medicines, especially as a theory had grown up to the effect that all diseases were caused by wrong proportions in the chemical substances that made up the body; and so the doctors, who were perhaps the best educated men of the time, worked at chemistry, to the great advantage of the science.

The medical chemistry of this period is often spoken of as Iatro-chemistry.

Little by little the explanation of what takes place when things burn became the great problem of the chemists. Fire has from time immemorial been used as a test for many things, and a rough classification of substances into (*a*) those that were altered in the fire, and (*b*) those that were not, had long been in use. Among the things that were altered may be mentioned wood, grease, oils, and many metals, such as iron, lead, magnesium; and the great question was: what is it that really happens to these things when they are burned? As long as chemists considered only the *kinds* of matter involved in these changes, no satisfactory explanation was forthcoming: it was when they began to consider the *quantities* used and produced that real progress was made. Let us examine this a little more closely.

When wood or other fuel is burned, it disappears more or less completely, nothing, or only a little ash, being left behind. It seems from this that burning consists in the breaking up of the burning substance, part or all of it disappearing.

Experiment.—Place a candle on one pan of a balance and carefully balance it by means of weights, shot, or sand on the other pan. Light the candle and allow it to burn for some time. It will be noticed that the pan holding the candle gradually rises, indicating loss in weight.

But let us examine some other cases of things altered by fire before making a final decision as to the true nature of this combustion.

Some of you have seen a blacksmith at work, and have noticed that after he has heated his iron very hot in the fire, some scaly material breaks off when he hammers it. If this "hammer scale" be carefully collected and put with the rest of the iron, it will be found that the whole weighs more than the original iron did. The same sort of thing happens when other metals are burned.

Experiment.—Place a metal plate or saucer on one pan of a balance (separating it from the pan by three or four little pieces of brick or stone, so that it will not injure the pan when it becomes hot); place on it about a tablespoonful of powdered magnesium metal in a conical pile, and balance it as was done in a previous experiment. Light the magnesium by means of a match or burner-flame.

Experiment.—Metallic lead or metallic tin may be highly heated for some time in a porcelain crucible. If the crucible and contents be weighed before heating and again after heating and cooling, gain in weight will be shown.

Between the years 1650 and 1775 the phenomena of combustion were explained by supposing that all combustible substances were made up of a peculiar something, a principle of combustibility, called phlogiston, combined with the ash, if any; and on burning, this phlogiston was supposed to escape. Hence the ash would be smaller than the original fuel:

Fuel = phlogiston + ash.

The same sort of explanation was employed in connection with the calcination of metals:

Metal = phlogiston + calx,

until it was observed that the calx was heavier than the original metal. The theory then became untenable.

Here then is a curious state of affairs—when fuels burn, there seems to be loss in weight; but when metals burn, there is very evidently gain in weight, and, therefore, it does not seem as though the two processes were similar and could be explained in the same way.

But if we pay a little closer attention to just what takes place, we shall find that we have made one of our experiments incompletely. You have often noticed that when the chimney is put on to a lighted kerosene lamp it becomes dimmed, or "steamed," for a while, and careful experiment shows that this is really due to tiny drops of water being deposited on the cold glass.

Experiment.—Light a candle and invert over it a dry, empty glass cylinder or bottle. Moisture will be deposited on the inside of the cylinder. It will soon disappear, owing to the warming up of the cylinder.

Further, someone discovered that this steam was not the only thing given off from the flame, but there was also produced a gas that would turn lime-water milky. This gas has been named carbon dioxide—we shall see why later.

Experiment.—If after performing the experiment just described above, the cylinder be removed from the candle, some lime-water be poured into it and it be quickly covered with the hand, or otherwise, and then shaken, the lime-water will become milky.

Now, in our experiment of weighing the burning candle, we did not catch the steam and carbon dioxide that were produced and keep them on the balance—it was something like trying to weigh a basket of kittens with the kittens jumping out one after the other and running off. Fortunately, a substance called caustic soda has been discovered which has the power of absorbing steam and carbon dioxide (holding the kittens); so, if we repeat our [illegible] experiment with the candle, using caustic soda in the proper way, we find that there is a gain in weight during the burning of a candle just as there was during the burning of a metal, the great difference being that the products of the burning in the first case, being gases, will escape unless prevented, while they will not in the second, because they are solids.

EXPERIMENT.—An argand lamp chimney has a piece of wire gauze fitted into it just above the constriction, is filled with sticks of caustic soda, and suspended from the top of the bow holding the balance pan, as shown in the figure. A little piece of candle is placed under it. (It is well to have a watch glass on the pan to catch the drippings from the candle and cylinder.) The whole is balanced by means of weights, or otherwise, and the candle is then lighted.

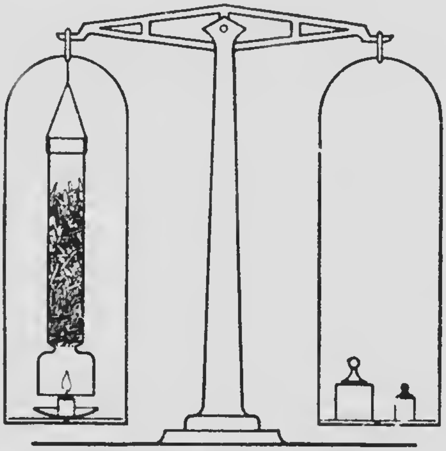

FIG. 1.

A great many very careful experiments have been made to find out whether matter really alters in weight when undergoing physical and chemical change, and all the results point to the fact that weight remains the same. This is stated as follows:

Law of Conservation of Matter.—*Matter cannot be created or destroyed; it can be changed from one form to another, but its quantity and weight remain constant.*

A more exact statement of this fundamental principle of physics and chemistry is as follows: **Law of Conservation of Mass.**—*The mass of a system is not affected by any physical or chemical change taking place within the system.*

There is a similar law relating to the other factor of all physical and chemical change, *i.e.*, energy: **Law of Conservation of Energy.**—*Energy may be changed from one form to another, but it cannot be created or destroyed.*

Now, if we keep this law in mind when thinking about the gain in weight in the experiments just made, we are forced to the conclusion that at the end of the experiment we are weighing more matter than we did in the beginning: that the water and carbon dioxide are the materials of the candle *plus* something else, and that the white ash formed when the magnesium burns, or the hammer scale formed on the iron, is the magnesium or the iron *plus* something else:

Hammer scale = iron + something else.

We at once want to ask two questions about this something else: What is it? Where did it come from? The second, being the easier, we will answer first.—It came from the air. We have two reasons for believing this: it cannot come from anywhere else; and, if we try to perform the experiment in a vessel from which all air has been pumped out (of course, making special arrangements for trying to light the candle or the magnesium), no chemical change takes place, nor any change in weight. (Compare, also, Lavoisier's experiment described below.)

It was much more difficult to answer the question: What is this something else? And for a long time it was very aggravating to think that water and carbon dioxide and magnesium-ash and hammer scale and a great many other things had this something locked up in them, but would not let the secret out!

An experiment has been defined as "a question put to nature in a language which she understands and in which she is capable of answering." And, at last, after someone had found the proper language in which to ask the question, nature answered what the something was: the proper experiment was hit upon, and it happened in this way. As we have already seen, iron, when highly heated in the air, forms a black calx, lead a brownish-yellow one, magnesium a white one, and so on. Mercury, if heated to the right temperature, very slowly forms a red calx (several days' heating is necessary to produce a satisfactory result). Now, there was a

Unitarian minister, named Joseph Priestley, who was very fond of making chemical experiments in his spare time, particularly with gases and things that would yield gases; and someone, knowing his fondness for examining new substances in this connection, sent him a sample of this red calx of mercury, or red precipitate, as it was called. On the 1st of August, 1774, a very important date in the history of chemistry, he heated some of it in a vial, and what was his amazement to see little drops of mercury produced on the sides of the vial just above the heated part and an invisible gas bubbling off from a tube fitted to the vial and dipping under water. He had broken the red precipitate up into the original mercury and the something else from the air which it had combined with when "burned," and the most striking property of the gas he found to be that it would cause a glowing splinter of wood, when plunged into it, to burst into flame and burn with great brilliancy.

EXPERIMENT.—In a hard-glass test-tube place a gram or two of mercuric oxide (red precipitate), and heat carefully. Note the appearance of drops of mercury on the upper part of the walls of the tube where they are not very hot. Introduce into the tube immediately after heating a glowing splinter (not flaming) of wood. What happens? Is the gas coming off combustible, or does it support combustion? How does it compare with air in this regard?

In accordance with a theory held at that time, Priestley called the gas "dephlogisticated air," but it was afterwards named oxygen by the great French chemist Lavoisier, who also showed that the weight of the red precipitate exactly equalled that of the mercury plus that of the oxygen :

$$\text{Calx of mercury} = \text{mercury} + \text{oxygen}.$$

This same sort of thing has since been shown to be true in the cases of the other calces and water and carbon dioxide, as we shall see later.

LAVOISIER'S EXPERIMENT.—Apparatus was used like that in the figure. The mercury in the retort was heated for 12 days, during which time the air in the bell-jar was reduced from 50 cubic inches to 42 cubic inches. 45 grains of red precipitate (calx of mercury) was formed on the surface of the mercury; and, when this was taken out of the retort, placed in a tube and heated, 8 cubic inches of gas was obtained—exactly the quantity which had been extracted from the air during the previous heating of the mercury. This proved very definitely that the "something else" concerned in the calcination of metals is derived from the air.

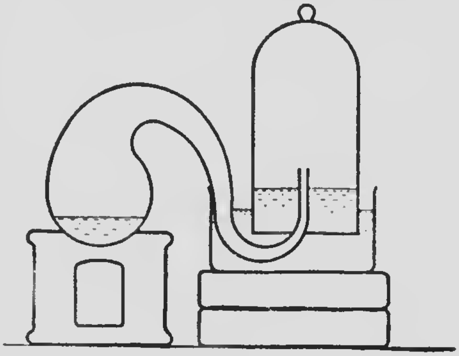

Fig. 2.

This experiment showed that about one-fifth (in this case, one-sixth, in other experiments a little more) of the air is used up when a metal burns in it. Priestley showed that the same thing is true when air is breathed. Further, when fuels are burned in the air, the result is the same. Not only does the same fraction of air disappear when metals are calcined in it, fuel burned, or animals breathe, but the four-fifths left in each case has the same properties—it will not support further burning or respiration. Hence, calcination, burning and respiration must be similar chemically.

By means of such experiments as those described above, especially by paying very close attention to the *quantities* of the substances used and produced, Lavoisier was able to overthrow the phlogistic hypothesis and introduce the new explanation of combustion, *i.e.*, combination with oxygen. The tremendous change in chemical opinions brought about by this work is often spoken of as the "chemical revolution."

From a consideration of the experiments described above, we may formulate the following definition:

Combustion *is an act of chemical union, accompanied by the production of heat and often of light.* One of the uniting substances is usually oxygen.

Red precipitate having been broken up into two constituents, mercury and oxygen, such questions as: Can mercury itself be broken up into two or more constituents? can oxygen be decomposed?, naturally arose. All attempts to do this have failed, and so we consider that these substances are undecomposable and we call them elements. Substances which can be decomposed are called compounds. We have therefore the following definitions :

An Element *is a substance which cannot be broken up into two or more substances of unlike properties.*

A Compound *is a substance that can be broken up into two or more substances of unlike properties.*

It is very important that these definitions should contain the phrase "of unlike properties," *or its equivalent*. A definition frequently given for the term element is "a substance that cannot be broken up." This is obviously incorrect. Copper is an element and a piece of copper wire can very easily be divided into many parts or pieces, be broken up. The same is true of any other element. The parts must be *of unlike properties*, if they are to satisfy the requirements of this definition.

Compounds must be carefully distinguished from mixtures. A compound is *a* substance, a mixture is not *a* substance but is made up of two or more substances which still preserve their identity, merely existing side by side, as in a mixture of grains of sugar and sand. A compound may be built up from two or more substances, as may also a mixture; but, in the case of the compound, the original substances lose their own properties, the compound having properties of its own; while in the case of the mixture, the original substances retain their own properties, those of the mixture being more or less the sum of these.

EXPERIMENT.—Mix two or three grams of fine iron filings with about twice its weight of powdered sulphur. Examine a little of the mixture carefully, drawing out some of the iron with a magnet. Place the rest of the mixture in a test-tube and heat carefully, noticing what happens, till the mixture is red hot. Cool, and examine the product. Find out whether it is magnetic.

Solutions are more or less intermediate between mixtures and compounds. A solution is *homogeneous throughout* and in this resembles a compound and not a mixture; but a solution is *variable in composition* and in this way resembles a mixture and not a compound. Solutions may be gaseous (air), liquid (brine), or solid (brass). The true nature of solutions is not at present satisfactorily understood.

Classes of Chemical Action.—The breaking down of red precipitate (mercuric oxide) into mercury and oxygen, and its formation from these two elements, are examples of two classes of chemical action which we shall often meet with; it will be well therefore to give the names by which they are known, and define the terms:

Analysis *is the breaking down of a compound into two or more substances of unlike properties.*

Synthesis *is the building up of a compound from two or more substances of unlike properties.*

There are two other classes of chemical action which we shall come across and define later on. They are *Replacement* (p. 42) and *Metathesis* (p. 105).

QUESTIONS

1. Mention some of the chemical changes that were earliest *of use to* the human race.

2. What chemical changes do you think were earliest *studied* by man?

3. What was the principal factor in bringing about the "chemical revolution" towards the end of the eighteenth century?

4. Why do you think that early investigators thought there was a loss in weight during the burning of a candle or ordinary fuels?

5. Criticise the following definitions, and correct them if necessary: (*a*) A compound is a substance that can be broken up into two or more parts; (*b*) A compound is a substance that can be broken up into different substances.

6. Distinguish between compounds and elements; between compounds and mixtures.

7. A wax match is placed close to the wick of a small candle which is then put into a large flask fitted with a stopper; the whole is balanced on a scale-pan. Then the stopper is removed, the head of the match touched with a red-hot wire and the stopper very quickly replaced. The match ignites the candle which burns for some time and then goes out. Why does it go out? Why do the flask and contents show no change in weight?

CHAPTER III

OXYGEN — OZONE

When making a special study of a chemical element, it is customary to consider, among other things, the history of its discovery, how it occurs in nature (*i.e.*, where we can get it), how it may be prepared (if it does not already occur pure), what its properties are (both physical and chemical), finally, what compounds it produces.

1. History
2. Occurrence
3. Preparation
4. Properties
5. Compounds

Of course, it is not necessary to go into all these details in the case of every element, but it is well to keep the outline in mind.

History.—Oxygen was discovered in 1774 by Dr. Joseph Priestley, as has already been described.

Occurrence.—A careful study of the various substances that surround us in nature shows that oxygen is very widely distributed. It forms [illegible] weight, about one-fifth of the air, eight-ninths of water, and [illegible] half of the solid crust of the earth. It also occurs in most animal and vegetable substances.

F. W. Clarke has calculated that the composition of the earth's crust, as far as it is known, is about as follows:

Oxygen . . .	49.98%	Calcium . . .	3.51%	Hydrogen . . .	0.94%
Silicon. . . .	25.30	Magnesium . .	2.50	Titanium . . .	0.30
Aluminium. .	7.26	Sodium. . . .	2.28	Carbon	0.21
Iron.	5.08	Potassium. . .	2.23	Other elements.	0.41

In the air, the oxygen is in the free state, *i.e.*, uncombined; in water, in the solid crust of the earth, and in animal and vegetable substances it is in combination with other elements.

Preparation.—To Priestley belongs not only the credit of the discovery of this gas and a number of others, but also the working out of a method for collecting gases free from air and other impurities, and thus enabling them to be studied with much greater accuracy than formerly, when they were generally collected in bladders, if collected at all. He used a tub, or other vessel capable of holding water, provided with a shelf pierced with holes and placed below the surface of the water. This arrangement is known as a pneumatic trough. By filling bottles or other vessels with water in the trough and then inverting them under the water and standing them on the shelf, over the holes, they may be very easily filled with gases by bringing under them the end of the tube delivering the gas, when this latter will bubble up through the water into the bottle without any air getting in. This is known as collecting gases over the pneumatic trough. (Sometimes mercury is used instead of water in the trough, which is then made small.)

As has already been pointed out, oxygen was first prepared pure by heating mercuric oxide (red precipitate).

$$HgO = Hg + O^*$$

This method is not generally used in the laboratory, because it is expensive and inconvenient. There are many other compounds which yield oxygen on heating, and the best of these is potassium chlorate.

$$KClO_3 = KCl + 3O$$

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* The meaning of these equations will be clear after studying Chap. VIII. They are introduced here because they will be of great value when reviewing.

It has further been found that if a little black powder called manganese dioxide be mixed with the potassium chlorate, the oxygen is given off at a much lower temperature, though the manganese dioxide is found after the reaction apparently quite unchanged. Why this happens we do not know. The mixture of potassium chlorate and manganese dioxide is called oxygen mixture.

The action of the manganese dioxide is an example of what is known as catalysis; the mere presence of a small amount of the catalyser—here, the manganese dioxide—seeming to be all that is necessary in order to exert a most marked influence on the speed of the reaction.

Experiment.—Fit a hard-glass test-tube air tight with cork and delivery tube, as in the figure. Mix about 10 gr. of potassium chlorate with about 6 gr. of manganese dioxide, both powdered. (As there are many black powders which form explosive mixtures with potassium chlorate, it is well to place a pinch of the mixture just made in a test-tube and heat it carefully to make sure that it is safe.) Place the mixture in the hard-glass test-tube, which it should about half fill. Arrange the apparatus as in the figure; fill a gas-bottle or cylinder to the brim with water, and, after having filled the pneumatic trough with water to a point about half an inch above the shelf, slide a piece of glass over the

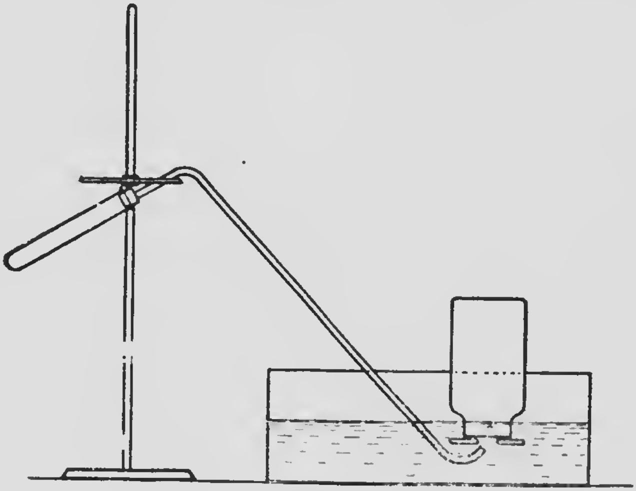

Fig. 3.

mouth of the bottle, so that no air is included, and set the bottle and plate, inverted, on the shelf of the trough and draw out the glass plate, being careful to keep the mouth of the bottle under the water all the time. (If no proper trough is available, a basin or shallow box may be used, with an inch or two of water in it, the delivery tube being thrust under the mouth of the inverted bottle which is held in an inclined position for this purpose.) Gradually heat the oxygen mixture in the test-tube and collect two or three bottles full of the gas. After a bottle is filled with the gas, it may be removed from the trough, if the latter is small, by slipping a glass plate under it, and placing it upright, still covered, on the table. Unless the glass plate and bottle are ground so as to fit tightly, the gas must be used almost immediately.

As soon as all the gas required has been collected, withdraw the delivery tube from the water while still heating the test-tube; otherwise water will be sucked back and the test tube broken.

The fused mass in the test-tube may, after cooling, be removed by filling the tube with water and allowing it to stand for some time. The mixture obtained in this way is filtered. This is done by folding a circular piece of white blotting paper (filter paper) into quadrants and then opening it out into a cone, with three thicknesses on one side and one on the other. This cone is then placed in a glass funnel and moistened with water. The liquid to be filtered is then carefully poured on to the filter, as indicated by the figure. The manganese dioxide will be found unchanged on the filter. Potassium chloride may be crystallised out from what runs through by slowly boiling it down in an evaporating dish.

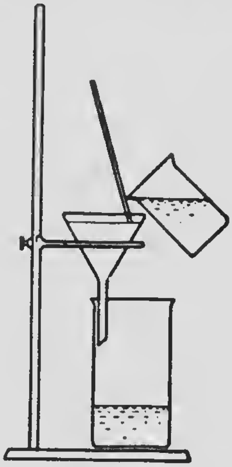

FIG. 4.

It is, of course, very important to know not only that potassium chlorate, on heating, yields oxygen and potassium chloride (the substance left behind in the test-tube with the manganese dioxide), but also exactly how much potassium chlorate yields how much oxygen and how much potassium chloride. Such experiments are rather too complicated to be attempted here, but they have been carried out over and over again, and it has been found that the proportions of the various substances are always exactly the same.

Properties.—*Physical Properties.*—If we examine the oxygen thus produced, we see that it is a gas and colorless. (When just collected, it sometimes contains a small quantity of very fine dust driven over from the test-tube; but this will settle out in a little while, leaving the gas perfectly transparent.) We may take a little of it into the nose and into the mouth, and find that it is odorless and tasteless. These are all the observations we can make with the unaided senses. By the use of the balance we find that oxygen is a little heavier than air; and by other experiments, that it is slightly soluble in water (about 3 volumes in 100, at ordinary temperatures).

1 litre of oxygen weighs 1.43 gr. It may be condensed to a bluish liquid by cold and pressure, and this liquid boils under atmospheric pressure at −182.5°. The specific gravity of the liquid is 1.13 (water = 1), and it is slightly magnetic. At a still lower temperature, the liquid freezes to a pale blue, snow-like solid.

The properties of oxygen given above are called its physical properties—they are the properties of the substance itself.

Chemical Properties.—The chemical properties of a substance are those concerned with its behaviour towards other substances—*i.e.*, how it combines with other substances to form compounds, or how it breaks up into simpler substances. This last, of course, oxygen cannot do, as it is an element.

As we have already seen, the air is partly oxygen, and it does not react with most other substances to any marked extent under ordinary conditions. Hence, oxygen is not a very active substance under ordinary conditions. At high temperatures, however, it is very active.

Experiment.—Light the end of a splinter of wood and blow out the flame, leaving a spark on the wood. Quickly remove the cover from the first bottle of oxygen collected and thrust this glowing splinter into it. Withdraw the splinter, blow out the flame, and again thrust it into the bottle. Do this several times, noting what happens. If the sides of the bottle had become dry before the experiment was performed, it will be noticed that they now become steamed—water is one of the products of the combustion of wood. If a little lime-water be poured into the bottle immediately after the wood has burned in it, the bottle be covered with the hand and shaken, the lime-water will turn milky. We shall see in a little while what this means.

The experiment just described shows, among other things, that oxygen makes burning possible—that it supports combustion; and also that the reaction goes on in the pure oxygen in a much more lively manner than it does in air—that it enlivens combustion. These facts are illustrated still further in the following experiments:

EXPERIMENT.—Set fire to a little sulphur in a deflagrating spoon; notice whether it burns slowly or rapidly in the air. Introduce the burning sulphur into one of the bottles of oxygen, keeping the bottle covered as much as possible. Notice what happens. When combustion becomes slow, remove the spoon, pour a little water into the bottle, close the mouth with the hand and shake. Is the gas produced by the combustion of the sulphur soluble in water? Why do you think so? Test the water solution with blue litmus. What happens?

EXPERIMENT.—Lower a piece of glowing charcoal in a deflagrating spoon into a third bottle of oxygen. What happens? Add a little water and shake as before. Test part of the water with blue litmus, and part with lime-water. Charcoal is a form of the element carbon. What do we now know of the composition of "the gas that turns lime-water milky?"

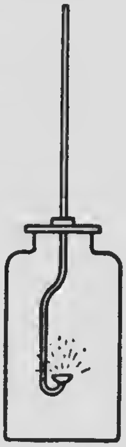
FIG. 5.

Certain substances that will not burn in air, of their own accord, will burn in oxygen. Thus, if a steel watch-spring be straightened out, tipped with sulphur, the latter ignited and the spring lowered into a jar of oxygen (some water being left in the bottom of the jar), the iron will be seen to burn, throwing off brilliant sparks, and the molten product drops into the water in the bottom of the vessel. If we carefully examine this product, we find it is our old friend hammer scale; so we have got at its composition. Iron and oxygen are elements, so the only reaction that can take place between them is one of combination,

$$3Fe + 4O = Fe_3O_4$$

Hence, we have proved the composition of hammer scale (calx of iron) by synthesis, *i.e.*, by building it up from its elements: it is oxide of iron. (To make the study complete, we should determine the relative quantities of the iron and oxygen. This has of course been done.)

An Oxide *is a compound of oxygen and another element.*

Oxidation *is the process of combining with oxygen.*

An Oxidising Agent *is a substance that will yield oxygen to another substance.*

Oxygen combines with almost all the elements, forming oxides of these elements.

The above experiments have shown us that, although oxygen does not act on most substances at ordinary temperatures, it does so at higher temperatures; experience also teaches us that it is much harder to start some substances burning than others; *i.e.*, the temperatures to which different substances must be raised before they will begin to burn vary very much from substance to substance, *e.g.*, phosphorus needs to be merely warmed, iron must be very highly heated.

The Temperature of Ignition *or* **Kindling Point** *of a substance is the lowest temperature at which it will burn actively.*

In order that a substance may burn, then, two things are necessary: First, something to support the combustion—generally air or pure oxygen; and, secondly, some part of the substance must be at a temperature equal to, or above, its particular kindling temperature. If the heat generated by the burning of this portion is sufficient to heat the next portion to the kindling temperature, and if more of the supporter of combustion is available, burning will continue. If, however, so much of the heat is dissipated as to prevent this, or if the supporter of combustion be no longer present, burning will cease. (It will, of course, also cease as soon as the supply of burning substance is exhausted.)

A slow oxidation may go on at a temperature very much below the kindling temperature—often at ordinary temperatures—as when iron rusts in the air, or oils harden (in paint), or wood decays. The slow oxidation of all these substances produces heat which, however, is generally dissipated as fast as produced. If, however, it cannot get away—as, for instance, inside a large pile of oily rags—the heat collects and the material slowly gets hotter and hotter till the temperature of ignition is reached and active burning begins. This phenomenon is often spoken of as spontaneous combustion.

An action similar to the burning of wood goes on very slowly in our own bodies: we inhale oxygen in the air we breathe and exhale carbon dioxide (the gas that turns limewater milky) and water vapor (which condenses when we breathe in very cold air). This oxidation is the source of our bodily heat and of our power of doing work. Oxygen, therefore, supports respiration as well as combustion. The dissolved oxygen in water supports the respiration of fishes (and is also of inestimable value in slowly burning up sewage and other impurities that get into natural waters, thus purifying them).

Oxygen enlivens respiration, and hence it is administered to people when they are very ill, and also to persons who are called on to make intense physical effort, as in athletics. In all these cases, great care should be taken to have the oxygen free from all injurious impurities; that made from potassium chlorate is liable to contain a trace of chlorine which has a very bad effect on the lungs.

It will doubtless have been noticed that the behaviour of most substances when burning in oxygen is similar to their behaviour when burning in air—only more energetic. Moreover, the products of combustion are the same in both cases (wood gives water and carbon dioxide, etc.). Now, from the experiments in oxygen, we know that the products are oxides—they cannot be anything else; we get the same products, *i.e.*, oxides, when the burning takes place in air: hence, air must contain oxygen.

Many substances will burn in chlorine, as we shall see; hence, we cannot say that mere supporting of combustion proves the presence of oxygen. The products of burning in chlorine are not oxides, or like them.

The fact that combustible substances burn much more energetically in pure oxygen than in air is easily understood when it is remembered that air is only one-fifth oxygen. Not only is it harder for the substance to find the oxygen as fast as it wants it, but the inert four-fifths of the air carry off a great deal of the heat produced and thus keep the temperature from getting very high. However, the *total* amount of heat produced when a certain quantity of any substance burns is always the same, whether it burn fast and produce a high temperature, or slowly and only a low temperature is attained on account of the dissipation of the heat.

Certain methods of producing oxygen, other than those mentioned above, are often used on the commercial scale. These may be summarized as follows:

Decomposition of acidulated water by electric current (electrolysis)

$$H_2O = 2H + O$$

Heating of barium dioxide (Brin's process)

$$BaO_2 = BaO + O$$

Intense heating of manganese dioxide

$$3MnO_2 = Mn_3O_4 + 2O$$

The slow evaporation of liquid air, most of the nitrogen and only a little oxygen going off during the first part of the evaporation, leaving most of the oxygen and only a little of the nitrogen.

(In the leaves of green plants, under the influence of sunlight, CO_2 is decomposed, its oxygen being returned to the air, as we shall see when speaking of starch.)

Ozone.—When electric sparks are passed through air or oxygen, something with a peculiar odor is formed. The same substance may be obtained as follows: In a glass jar, or wide-mouthed bottle, place a clean piece of phosphorus about the size of a marble and partly cover it with water. (Cut the phosphorus under water and lift it with forceps, not with the fingers.) Place a piece of paper or card over the mouth of the jar. After some minutes the gas in the jar will be found to have a peculiar odor, and paper saturated with a solution of starch and potassium iodide will be quickly turned blue if placed in the jar. The substance produced in this way is called ozone; it is a gas, colorless, with a strong odor, and it has been shown that it is a peculiar form of oxygen, more dense than the ordinary form.

Its density is 48, while that of ordinary oxygen is 32 (H = 2). As we shall see later, the molecule of oxygen is composed of two atoms: that of ozone is composed of three atoms.

$$3O_2 = 2O_3$$

Ozone has chemical properties similar to those of oxygen, but it is more active. It is reconverted into oxygen by heating to 300°.

As we continue our study of chemistry, we shall find several examples of elements that exist, like oxygen, in two or more very different forms; hence, we have a term to express this.

Allotropy *is the property exhibited by certain elements of existing in two or more distinct forms. Such elements are said to be allotropic.*

QUESTIONS

1. Describe the preparation of oxygen, *with a sketch of the apparatus* employed.

2. Why does a sudden puff of fresh air put out the flame of a candle?

3. Why should oily waste be put into metal boxes and not thrown into corners?

4. Give two reasons for the extinguishing of a fire when plenty of water is poured on it.

5. When we wish to light a hard-coal fire, why do we use (*a*) paper, (*b*) kindling-wood (or charcoal)? Why is it that the stove itself does not take fire?

6. Do we know of any examples of combustion that do not produce light? Any light not due to combustion?

7. A little mercury is placed in a large flask which is then sealed up and weighed. The whole is heated for some days, till the mercury is partly converted into oxide, and then it is weighed again. No change in weight has taken place. How do you account for this? The flask is then carefully opened and again weighed, and a gain in weight is observed. How do you account for it?

8. Describe, *with a figure*, the method of collecting gases over the pneumatic trough.

9. How might the experiment of preparing oxygen from potassium chlorate be carried out quantitatively?

10. List the properties of oxygen, thus: *A*, Physical properties, 1, 2, &c. *B*, Chemical properties, 1, 2, &c.

11. Why should we expect to find oxygen colorless, odorless, tasteless?

12. Taking several of the experiments in this chapter together, what do they teach us as to the chemical composition of wood?

13. Cite some examples of oxidation from the experiments in this chapter.

14. Criticise the statement: The temperature of ignition (kindling temperature) is the temperature at which a substance will burn.

15. Compare, in tabular form, the burning of sulphur, iron and carbon in oxygen and also in air, with the products obtained. What does this suggest as to the chemical composition of the air?

16. Why is it wrong to write $KClO_3 = KCl + O_3$?

17. In preparing oxygen from chlorate of potash, three bottles of the gas are collected. Which bottle do you think contains the purest oxygen, and why?

18. The rusting of iron is really a case of combustion. Why does the iron not get hot?

19. When the end of a splinter of wood is lighted, why does not the whole splinter burst into flame—why does the flame creep slowly along the wood?

(*The following calculations should be left till after Chapter VIII has been studied.*)

20. 36 grs. of mercuric oxide is heated. How much oxygen is given off?

21. How much mercuric oxide must be heated in order to obtain 4 grs. of oxygen?

22. With how much oxygen can 100 grs. of mercury combine to form mercuric oxide?

23. A gas-holder has a capacity of 100 litres. How much chlorate of potash must be heated in order to produce enough oxygen to fill it under standard conditions? At 740 mm. and 15°?

24. 5 grs. of iron is burned in oxygen. What is the weight of the iron oxide produced?

25. With what volume of oxygen can 12 grs. of carbon combine to form CO_2? What will be the volume of the CO_2.

26. If the price of potassium chlorate is 25c. per kilo and that of mercuric oxide $1.75, what will it cost to prepare 1,000 litres of oxygen from each?

CHAPTER IV

HYDROGEN

History.—Long ago, chemists in their random mixing of various solids and liquids had come across cases where gases were produced, and sometimes they found that these gases could be set on fire. Such a gas was obtained, for instance, when oil of vitriol (sulphuric acid) was poured on to iron—and this gas was called "inflammable air." Sir Henry Cavendish, an Englishman, made a special study of it in 1766, and later noticed, among other things, that water was produced when it burned. Lavoisier studied this still further and named the gas hydrogen, from two Greek words meaning water generator.

Occurrence.—Hydrogen does not occur free (uncombined) to any important extent in nature, but in combination it forms about one-ninth of water, so there is plenty of it to be had. Further, as we shall see later, it occurs in combination in all acids and in almost all animal and vegetable substances as well as in some other things.

Preparation.—Hydrogen is prepared for experimental purposes either from water or from acids :

From water :	by action of metals
	by action of electric current
From acids :	by action of metals

To prepare hydrogen from water, which is a compound of hydrogen and oxygen, we may present something to the water that will take away the oxygen and leave the hydrogen by itself. Certain metals have the necessary desire for oxygen, some of them acting satisfactorily at ordinary temperatures and others only at high temperatures. Thus, if a piece of metallic sodium about the size of a pea be dropped on some water in a dish, it will be seen to move about rapidly on the surface of the water, gas being given off with effervescence ; if a lighted match or taper be touched to the gas, the latter will take fire.

$$Na + H_2O = NaOH + H$$

Certain other metals will decompose water at high temperatures. Thus, if steam be driven into one end of an iron or porcelain tube filled with tacks or iron shavings, and kept at a high temperature, hydrogen may be collected at the other end of the tube, while the iron becomes covered with hammer scale.

$$3Fe + 4H_2O = Fe_3O_4 + 8H$$

A similar action, rust being formed, takes place at ordinary temperatures, only *extremely* slowly.

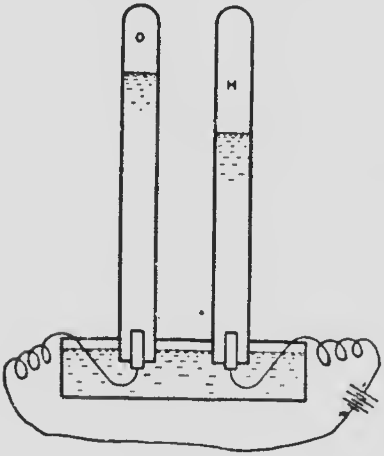

Fig. 6.

If an electric current be passed through water (containing a little sulphuric acid), hydrogen is given off at one pole and oxygen at the other. The apparatus employed may be of various forms, one of the simplest patterns being that illustrated in the figure. The wires coming from a battery of four or five cells, arranged in series, terminate in pieces of platinum foil (which is not acted upon during the experiment, as copper would be), and these pieces of foil are placed, as indicated, just in the openings of two tubes filled with water containing about one-tenth of its weight of sulphuric acid and inverted in a dish containing more of the same solution. On turning on the current, bubbles of gas will collect on the electrodes (foil) and break away from them, rising into the tubes. It will be noticed that half as much gas collects in one tube as in the other; and, by applying proper tests (such as introducing a glowing wood splinter), the gas in smaller volume is found to be oxygen. The other gas is hydrogen.

The most convenient method of preparing hydrogen for laboratory purposes is by acting on an acid, such as sulphuric or hydrochloric, with a metal such as zinc or iron.

$$Zn + H_2SO_4 = ZnSO_4 + 2H$$

Hydrogen mixed with air explodes on ignition; *therefore. do not bring a flame near any apparatus generating hydrogen,* unless special precautions have been taken.

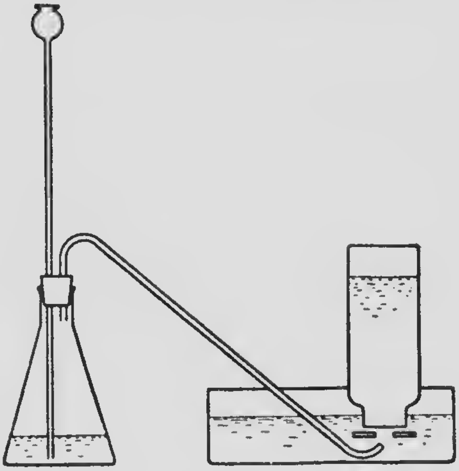

Fig. 7.

Experiment.—Fit up an apparatus, such as is illustrated in the figure, being very careful that the joints are air-tight. Place in the flask a small handful of granulated zinc and pour down the thistle-funnel enough dilute sulphuric acid to cover it, taking care that the end of the thistle-funnel is covered also. Allow the gas to come off until the air has been displaced from the apparatus, and then collect a test-tube full over the pneumatic trough, light it, and observe whether there is a slight explosion or not. If there is none, collect two bottles full. The $ZnSO_4$ (zinc sulphate) formed remains dissolved in the water.

Properties.—*Physical Properties.* If we examine the substance produced by the action of the zinc and sulphuric acid, we observe first, that it is a gas, and that it is colorless. Prepared from ordinary zinc, which is impure, it has a slightly disagreeable odor, but hydrogen itself has no smell or taste. (It is not poisonous, but of course a person could not live in it for any length of time, as he needs oxygen.)

Hydrogen is the lightest substance known ; one litre of it, at 0° and 760 mm. (see p. 45), weighs 0.09 gr. On this account it is sometimes used for inflating balloons, though the cheaper coal-gas is generally employed.

EXPERIMENT.—If a glass tube about 10 cm. long, and loosely filled with cotton wool, be connected to the delivery tube of the generator used above and a clay tobacco-pipe to this, soap bubbles may be blown with the hydrogen, and they will float in the air.

Hydrogen has been liquified and solidified. Its melting point is −260° and it boils, under atmospheric pressure, at −252.5°.

Chemical Properties.—At ordinary temperatures, hydrogen is quite inactive. If, however, it be heated, it will burn in air or in oxygen.

$$2H + O = H_2O$$

EXPERIMENT.—Remove one of the bottles full of hydrogen from the trough (Exp. p. 39), and, holding it upside down, thrust a lighted splinter or taper up into it. Does the taper continue to burn? Is it lighted again as you withdraw it? Does hydrogen support combustion ? Does it burn ?

Draw a glass tube out to a jet and substitute it for the delivery tube of the generator. Having wrapped a towel round the generator, light the gas escaping from the jet and note the color of the flame. Hold a dry beaker over the flame. What happens? What does this behaviour indicate?

Hydrogen does not support combustion, but it burns with a pale blue, very hot flame, producing water. (The yellow color of the flame burning at the jet in the experiment is due to a trace of vapor of sodium from the heated glass.)

In the experiments just described, the hydrogen gets its necessary oxygen slowly; if, however, we mix the hydrogen with oxygen (or air) first and then ignite, the combustion takes place so exceedingly rapidly that an explosion is the result.

Experiment.—Fill a strong glass cylinder two-thirds full of hydrogen and then pass in one-third of oxygen (or, use one volume of hydrogen to two volumes of air). Roll a towel round the cylinder (in case it should break) and then bring a light to the open end.

There are two principal kinds of explosions—those produced by the ignition of an intimate mixture of a combustible and a supporter of combustion (hydrogen and air, coal dust and air, flour and air, gunpowder) and those produced by the very sudden decomposition of certain compounds, such as nitro-glycerine. In both cases, large quantities of gases at high temperatures, and therefore enormously expanded, are produced.

If a flame of burning hydrogen be supplied with pure oxygen, as in the oxy-hydrogen blowpipe (see figure), a very high temperature is produced: the flame will melt platinum. If such a flame be directed against a piece of quick-lime, which is infusible, the lime is so highly heated that it gives out a powerful white light. This is known as the lime-light (calcium light, Drummond light), and was formerly much used in theatres, in magic lanterns, etc. It has been almost altogether superseded by the arc light.

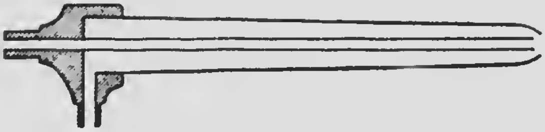

Fig. 8.

The last two experiments show that hydrogen at a high temperature combines eagerly with oxygen. Indeed, under such conditions, its affinity for oxygen is so great that it can extract it from many of its compounds. This reaction is known as reduction.

Reduction *is the act of extracting oxygen from a compound that contains it, and the substance that is capable of doing this is called a* **Reducing Agent.**

Experiment.—Place some copper oxide in a hard-glass tube and support it above a burner. Connect this tube with a hydrogen generator, as in the figure, and heat the tube while the hydrogen is passing. (The usual precautions against explosion must be taken.) The copper oxide is reduced to metal, as can be seen by the change in color, and water is produced at the same time.

$$CuO + 2H = H_2O + Cu$$

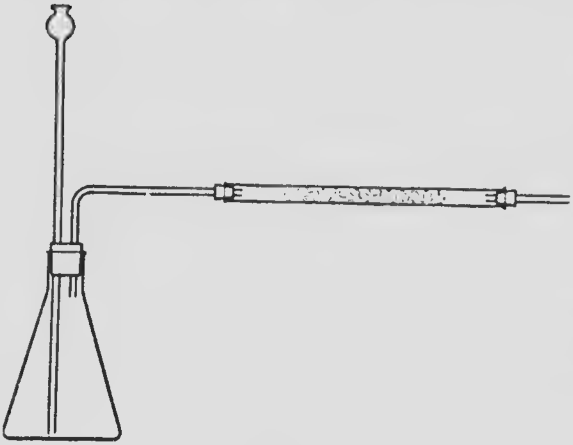

Fig. 9.

We have already noticed two classes of chemical action, *i.e.*, analysis and synthesis—this chapter furnishes us with several examples of a third class, *i.e.*, replacement. In the action of sodium on water, of zinc on sulphuric acid, of hydrogen on copper oxide, this sort of reaction takes place and it may be defined as follows:

Replacement, *or substitution, is the action that takes place between a chemical compound and another substance, generally an element, whereby this other substance combines with a part of the compound, liberating the rest*—the other substance takes the place of a portion of the compound.

QUESTIONS

1. What did the old chemists mean by "inflammable air?" Why did they call it so?

2. How would you explain the presence of some hydrogen in the "air" obtained from the coils of a hot-water furnace?

3. Why must all the air be driven out of the hydrogen generator before the issuing hydrogen is ignited? Why do we wrap a towel round the flask? Is hydrogen itself explosive?

4. Would hydrogen make a good substitute for coal-gas (*a*) in an ordinary lighting burner, (*b*) in a burner fitted with an Auer-light mantle, (*c*) in a gas stove? Why?

5. Sometimes fearful explosions occur in flour mills; what do you think is the cause? Might some of the explosions in coal mines be due to a similar cause?

6. If your stock of metallic sodium took fire, would you use water or sand to extinguish it? Why?

7. When hydrogen is prepared by the action of zinc on sulphuric acid, what else is formed? What becomes of it?

8. Potassium (K) reacts with water in the same way that sodium does; write the equation representing the reaction.

9. Compare oxygen and hydrogen as to (*a*) occurrence, (*b*) properties.

10. In the apparatus pictured in Fig. 7 why should the thistle-tube extend almost to the bottom of the flask?

11. How could you distinguish a bottle of oxygen from one of hydrogen?

12. Compare oxidation and reduction. Is the one just the opposite of the other?

13. Why is hydrogen called a reducing agent? Iron? Examples.

(*The following calculations should be left till Chapter VIII has been studied.*)

14. How much zinc and sulphuric acid must be used to produce 100 grs. of hydrogen? (Note: the two chemicals must be reported separately.)

15. What volume of hydrogen could be produced by acting on 23 grs. of sodium with water?

16. How much water could 92 grs. of sodium decompose?

17. A balloon has a capacity of 1,000 litres. How much zinc and sulphuric acid will be required to produce sufficient hydrogen to fill it at 750 mm. and 18°? With zinc at 15c. per pound and iron at 4c., what would be the cost of each metal for the above filling?

CHAPTER V

THE GAS LAWS AND THE MOLECULAR THEORY

It is not a very easy matter to weigh gases; hence, when we wish to determine their quantity, we generally do it by measuring their volumes. It needs only a little observation, however, to show that the volume of any particular quantity of gas does not always remain the same—unless it is hermetically sealed up — but that it varies with changes in temperature and pressure. These changes in volume are physical changes, and their study belongs to the science of physics; but a knowledge of them is of such great importance to chemists that we must very briefly review them here, though, for a detailed discussion of them, books on physics must be consulted.

The pressure of gas is usually measured, for scientific purposes, by means of a barometer and is expressed in millimeters of mercury, the average, or normal, pressure of the atmosphere at sea level being equivalent to 760 mm. of mercury and being called **Standard Pressure (S.P.).** If, now, we measure the volume of a certain quantity of gas under this pressure, then double the pressure and measure the volume again, we find that the volume is half what it was before; and this is true of all variations in pressure and volume. Thus:

P.	V.
190 mm.	4
380 “	2
760 “	1
1520 “	$\frac{1}{2}$
3040 “	$\frac{1}{4}$

Now, when we discover some invariable relation, or mode of behaviour, in nature, we express it in the form of a concise statement, which we call a law, and the law concerning the relation between the volume of a gas and the pressure upon it was discovered by Robert Boyle in 1660. Hence,

Boyle's Law.—*The volume of a gas is inversely proportional to the pressure under which it exists.*

By means of this law, we can find out by simple calculation what the volume of a gas measured under one pressure would become under any other pressure. For, if we multiply the volume by the pressure under which it is measured, we find what it would be under 1 mm. pressure; and then, by dividing this volume by the new pressure, we obtain the new volume.

EXAMPLE.—A gas measures 25 cc. under a pressure of 753 mm. What would it be under a pressure of 760 mm.?

If the pressure is reduced to $\frac{1}{753}$ of what it was, *i.e.*, to 1 mm., the volume would become 753 times as large, *i.e.*, 25×753. If now the pressure be increased 760 times, *i.e.*, to 760 mm., the volume will become $\frac{1}{760}$ of what it was at 1 mm., *i.e.*, $25 \times 753 \times \frac{1}{760}$, or $25 \times \frac{753}{760}$.

We see, therefore, that in reducing the volume of a gas from what it is under one pressure to what it would be under another, we multiply by a fraction, the numerator of which is the original pressure and the denominator the new.

Now let us see how the volume of a gas is affected by change in temperature. It has been agreed among physicists and chemists that 0°C. should be regarded as **Standard Temperature (S.T.)** for these purposes, and careful measurements have shown that if a gas at 0° be raised one degree in temperature, its volume increases $\frac{1}{273}$ of what it was at zero (the pressure, of course, remaining constant). If it be heated from 1° up to 2°, its volume again increases $\frac{1}{273}$ *of what it was at zero*; and the same sort of thing happens if the gas at 0° be cooled—it contracts in the same ratio. So we can again generalise, and thus obtain—

Charles's Law *or* **the Law of Gay-Lussac.**—*The volume of a gas increases (or decreases) $\frac{1}{273}$ of its volume at zero for every degree rise (or fall) in temperature.*

(It must be carefully observed that it is $\frac{1}{273}$ of its volume *at zero.* Thus, if a gas at 20° is heated to 21°, it will not expand $\frac{1}{273}$ of what its volume is at 20°, but $\frac{1}{273}$ of what its volume would be at 0°.)

Suppose now that we start with a certain volume of gas at 0° and cool it to − 1°, it will contract $\frac{1}{273}$ of its volume; if we cool it to − 2° it will have contracted, in all, $\frac{2}{273}$ of its original volume. Finally, if we could cool it to − 273° it would (theoretically) lose $\frac{273}{273}$ of its original volume, *i.e.*, its volume would become 0. As its volume cannot become less than 0, we argue that there is no temperature below − 273°C. This is *absolute* cold, and the temperature is called *Absolute Zero.* A thermometer-scale, with degrees the same size as centigrade degrees and this point labelled zero, is called the *Absolute Scale.* 0°C. becomes 273° on the absolute scale and 100°C., 373° absolute.

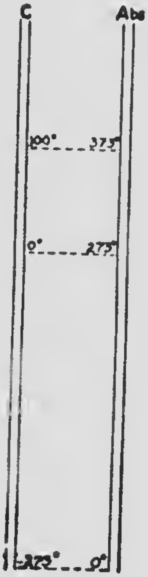

FIG. 10.

This may be formulated as follows:

$$\text{Abs.}^\circ = \text{C.}^\circ + 273^\circ \quad \text{or} \quad \text{C.}^\circ = \text{Abs.}^\circ - 273.^\circ$$

Further, let us consider a volume of gas which, for convenience in calculation we choose as 273 cc., at 0°C., *i.e.*, 273° Abs. If we raise the temperature 1°, the volume will be 274 cc., and so on; and similarly for lowering of temperature, as indicated in the table:

Vol.	C.	Abs.	Vol.	C.	Abs.
276 cc.	3°	276°	272 cc.	− 1°	272°
275 "	2°	275°	271 "	− 2°	271°
274 "	1°	274°	270 "	− 3°	270°
273 "	0°	273°		etc.	

We see at once that the number of cc. of gas is the same as the number of degrees on the absolute scale. Thus, we get a new enunciation for the

Law of Charles or of **Gay-Lussac.**—*The volume of a gas varies directly as its absolute temperature.*

Now, if we want to find out what the volume of a gas measured at one temperature will become if the temperature be changed, we proceed as follows: First, see that the temperatures are on the absolute scale (if expressed in Centigrade, add 273°); secondly, divide the volume of the gas by its original temperature to find what it would be at 1° Abs. and then multiply this by the new temperature.

EXAMPLE.—A gas measures 31 cc. at 18°C.; what will be its volume at 0°C.?

18°C. = 18° + 273° = 291° Abs. and 0°C. = 273° Abs.

31 ÷ 291 is what the volume will be at 1° Abs.

(31 ÷ 291) × 273, or 31 × $\frac{273}{291}$, is what it will be at 273° Abs. = 0°C.

Thus we see, that to reduce a volume from one pressure to another we multiply by a fraction made up of the old and new pressures; and for change in temperature, we use a fraction made up of the old and new temperatures (on the absolute scale). These corrections may be applied independently or both together. In applying these fractions, however, we must do so thoughtfully and not mechanically. Thus: A gas measures 927 cc. under a pressure of 775 mm. and at a temperature of 18°C. What will be its volume under standard conditions, at S.T.P. (*i.e.*, 760 mm. and 0°C.)? Suppose we are not sure of our equation and cannot remember whether we should multiply by $\frac{775}{760}$ or $\frac{760}{775}$. Think of it in this way: The pressure is to change from 775 to 760 mm., *i.e.*, is to become less; then the volume of the gas will become greater; so we must multiply by a fraction that will make it greater, *i.e.*, $\frac{775}{760}$ Similarly with the temperature:

from 18°C. (*i.e.*, 18 + 273 = 291 Abs.) to 0°C. (273 Abs.) is a lowering of temperature, accompanied by a contraction of the gas; therefore our fraction must be less than 1, *i.e.*, $\frac{273}{291}$. The whole thing works out as follows:

$$\text{Vol.} = 927 \cdot \frac{775}{760} \cdot \frac{273}{291}$$

Where gases are collected over water, they always contain a certain quantity of aqueous vapor, depending on the temperature; and the tension (pressure) of this vapor, plus the actual pressure of the gas, is the pressure which we measure (indirectly) by means of the barometer. In accurate work, the tension of aqueous vapor (taken from a table) should be deducted from the barometric pressure in order to obtain the correct pressure of the gas. Under laboratory conditions, this will be only about 2% of the total pressure; hence, the error introduced by neglecting the tension of aqueous vapor may be ignored in ordinary work.

In addition to the two laws mentioned above, there is another very striking fact connected with all gases. Suppose we have a cylinder full of hydrogen and another full of air, and place these mouth to mouth, the one full of the lighter hydrogen being above, and leave them like this for a little while; then, if we examine the gas in each cylinder, we find that the air and hydrogen have mixed completely, so that the whole mass of gas is uniform throughout, half of the lighter hydrogen having passed into the lower cylinder, while half the heavier air has passed into the upper. This process, by virtue of which gases mix with one another, and pass spontaneously through small openings, is known as *diffusion of gases*, and it is found that the lighter a gas is, the faster it diffuses. It is on account of this (in part) that the composition of the atmosphere is kept so nearly uniform, as we shall see later; and also, this explains why it is so hard to keep any particular gas pure and free from other gases, especially from air.

We have just been considering two very important natural laws concerning gases, one dealing with the relation between the pressure and volume of the gas, and the other with the relation between the temperature and volume.

A Natural Law may be defined as *a constant or uniform relationship, or mode of behaviour, observed in nature, and expressed in the form of a concise statement.* It is a generalisation of a very large number of facts.

It is very interesting to discover these relationships, and scientific men are constantly trying to detect more of them, because they firmly believe that the whole of nature is most intimately inter-related. A knowledge of facts and laws alone, however, is not satisfying to the mind. It is very interesting to know *how* things happen, but something in us makes us constantly ask *why* they happen as they do. We know *how* gases behave with regard to pressure and temperature; but *why* should they do it? What is there in the nature of all gases that seems to force them all to behave alike with respect to these two conditions?

Having failed to find any answer to this question by examining gases more closely, we *imagine* a cause—we set our minds to work and produce a mental picture of the structure of gases such that, if gases are really like it, then they *must* behave as they do. Such *mental pictures, designed to explain certain laws,* are at first called **Hypotheses**; and if, after being carefully compared with all the facts relating to them, they still seem to be rational and useful, then we call them **Theories.** (A theory is a hypothesis which has grown up and passed its examinations!)

With regard to gases, then, people who have studied the subject most carefully have put forward what is known as the

Molecular Theory: *All gases are made up of separate particles, called molecules. These molecules are in a state of rapid motion.*

Although a bottle full of air or oxygen seems to be perfectly uniform and quiet throughout, we must think of it as really made up of an enormous number of very small particles with, comparatively speaking, very large spaces between them and these particles rushing and bounding and whirling about all the time, bumping against one another and against the walls of the vessel which contains them, thus exerting pressure upon it. This motion of the molecules is heat, and is the cause of diffusion. In a hot body the motion is very rapid, in a cool body it is less rapid, in a body at absolute zero there is no motion at all—hence, nothing can be colder (stiller) than absolute zero. The very essence of the theory is that matter has a sort of granular, or *discontinuous* structure.

A Molecule *is the smallest quantity of a substance that can exist by itself* (*i.e.*, in the free, or uncombined, state). The word "molecule" is derived from the Latin *molecula*, a little heap, because a molecule is made up of a little heap of atoms, as we shall see later on. We have molecules of elements, in which the component atoms are all alike, and molecules of compounds, in which the atoms are different.

It should be observed that the smallest quantity of oxygen, for instance, that can exist by itself (*i.e.*, in a *free* state), is two atoms, O_2; whereas, the smallest quantity of oxygen that can exist in *combination* is half of this, *i.e.*, one atom, O.

The molecular theory is applied also to liquids and solids.

All the molecules of any one sort of substance must be exactly alike, because any one sort of substance always has the same properties, and therefore, it cannot be molecularly coarse-grained in one sample and fine-grained in another.

Although this molecular view of matter may not seem very sensible just at first, the more we study the facts of nature the more we are convinced that this picture is true.

In order to make the theory thoroughly satisfactory, *i.e.*, have it explain the laws as completely as possible, it was necessary to make a little extension to it, and this is known by the name of the Italian who first put it forward.

Avogadro's Hypothesis.—*Equal volumes of all gases, under similar conditions of temperature and pressure, contain equal numbers of molecules.* That is, when temperature and pressure are alike, there is the same amount of crowding in all gases. If one litre of hydrogen at a certain temperature and pressure, contains x molecules, then one litre of oxygen, or of air, or of any other gas, at the same temperature and pressure, contains x molecules.

This is often spoken of as Avogadro's *law*, but it is not a law at all; it is not a condensed statement of facts that we know; it is a guess, an imaginary picture, as to what we suppose. Further, although still spoken of as a hypothesis, it has long ago graduated to the rank of a theory.

Although it is impossible to find out the actual weights of molecules by experiment, we can determine their relative weights by making use of Avogadro's hypothesis. A litre of hydrogen weighs 0.09 gr., and a litre of oxygen weighs 1.43 gr., *i.e.*, x molecules of oxygen weigh 16 times as much as x molecules of hydrogen. Therefore, each molecule of oxygen must weigh sixteen times as much as each molecule of hydrogen. Hydrogen being the lightest substance known, was chosen as the standard, and, for a reason that will appear later, its molecule was said to weigh 2; then the molecule of oxygen must weigh $16 \times 2 = 32$. (Some of the numbers used here will not appear quite correct; this is because we do not calculate out to many places of decimals. Thus, the weight of a litre of hydrogen is really 0.089947 gr., and not 0.09 as we have used it.)

If 1 litre of hydrogen weighs 0.09 gr. and 1 litre of oxygen weighs 1.43 gr., then 22.4 litres of each will weigh 2 gr. and 32 gr., respectively. But, as we have just seen, these numbers represent the molecular weights of hydrogen and oxygen; and what is true of them in this respect is true of all gases. Therefore we may say that *the weight in grams of 22.4 litres of any gas, under standard conditions, is numerically equivalent to its molecular weight.*

Gas	Wt. of 1 Litre	Wt. of 22.4 Litres	Mol. Wt.
Ammonia	0.7617 gr.	17 gr.	17
Carbon dioxide.	1.9641 "	44 "	44
Carbon monoxide	1.2499 "	28 "	28
Chlorine	3.1650 "	71 "	71
Hydrochloric acid. . . .	1.6275 "	36.5	36.5
Hydrogen	0.0899 "	2 "	2
Nitrogen	1.2501 "	28 "	28
Oxygen	1.4285 "	32 "	32
Water (Steam).	0.8036 "	18 "	18

The Gram-Molecular Volume (G.M.V.) *is 22.4 litres, so-called because the weight in grams of this volume of any gas (under standard conditions) is numerically equivalent to its molecular weight.*

The molecular weight of a gas, then, is ascertained by determining the weight in grams of 22.4 litres of it under standard conditions of temperature and pressure (or under some other conditions and then calculating to standard conditions).

There are many indirect methods of determining molecular weights, including those of liquids and solids, but they cannot be discussed here.

The density of any gas compared with air, may be determined by comparing the weight of 22.4 litres of that gas (its molecular weight expressed in grams) with the weight of 22.4 litres of air, which is 28.8 grs. This number is often very useful, as it dispenses with the necessity of committing to memory a number of densities.

Hydrogen = 2 was the original standard for molecular weights. For reasons that cannot be discussed in this place, oxygen = 32 is the one now generally adopted. As, however, this makes a difference in any particular case, only in decimals, it need not concern us here.

It is impossible to say when the molecular theory was first enunciated, or by whom. Certain ancient Greek philosophers taught something like it, using, however, the term atom instead of molecule. The theory then went out of existence for hundreds of years, as far as natural science was concerned, but was re-enunciated in an altered form about the beginning of the 19th century. For a long time there was great confusion between it and the atomic theory, until finally the tangle was straightened out mainly through the teaching of the

Italian professor of chemistry, Cannizzaro, about 1860. It is interesting to note that, starting with the molecular hypothesis, Boyle's law, Charles's law and Avogadro's hypothesis may, by the principles of mechanics, be deduced as necessary consequences.

As this chapter has been rather a long one, and as its subject matter is exceedingly important for our whole study of chemistry, it will be a good thing to draw up a logically arranged outline, so that we may get a more or less complete mental picture of it and, at the same time, get an elementary idea of part of the scientific method. The details can, of course, be filled in by referring back to what has already been said.

Observations:	All changes undergone by matter.
Classification:	Bringing together all changes in the volumes of gases due to changes in pressure and temperature.
Generalisations:	Pressure—Boyle's law.
	Temperature—Charles's law.
Speculation:	Reasons for these laws—Molecular theory.
	Avogadro's hypothesis.
Deduction:	Method of determining molecular weights.

QUESTIONS

NOTE.—*All temperatures are centigrade unless otherwise stated.*

1. What uniform methods of behavior are exhibited by all gases?
2. Define the term law, as used in science.
3. What is meant by standard temperature, by standard pressure? What does S.T.P. mean?
4. What is meant by the absolute scale of temperature? What is the equivalent of absolute zero on the centigrade scale and of 0° centigrade on the absolute scale?
5. Reduce the following temperatures to their equivalents on the other scale: – 25°C., 16°C., 100°C., 27° Abs., 376° Abs. Are there any minus temperatures on the absolute scale? Why?
6. Define the terms hypothesis and theory as used in science.
7. Why is the volume 22.4 litres of so much importance in chemistry? What name is given to it?
8. What is the meaning of G.M.V.?
9. A steel cylinder has a capacity of 50 litres. It is filled with oxygen under a pressure of 150 lbs. to the square inch (15 lbs. = 1 atmosphere). What weight of oxygen does it contain?

10. How is the molecular weight of a gas determined? Upon what hypothesis does this determination depend?

11. Give an outline of part of the scientific method.

12. What is meant by the term diffusion of gases?

13. Why does hydrogen leak so easily through badly made joints?

14. What surprising conception of matter is introduced by the molecular theory?

15. Enunciate the molecular theory.

16. For what purpose was the molecular theory devised?

17. A certain volume of air measures 1 litre under 738 mm. pressure. What will be its volume under 769 mm.?

18. A quantity of hydrogen measures 320 cc. under 750 mm. pressure. What would its volume be under normal pressure?

19. Reduce the following gas volumes to S.P.: (*a*) 150 cc. at 380 mm., (*b*) 279 cc. at 1520 mm.

20. A certain quantity of oxygen measures 1 litre at standard pressure. At what pressure will its volume be doubled?

21. Some air is measured in a tube under normal pressure; then a total pressure of 5 atmospheres is put upon it. What relation does its volume now bear to the original volume?

22. A certain volume of air measures 1 litre at 17°. What will be its volume at 34°?

23. A quantity of hydrogen measures 320 cc. at 20°. What will be its volume at standard temperature?

24. Reduce the following gas volumes to S.T.: (*a*) 150 cc. at 18°, (*b*) 279 cc. at 300°.

25. A certain quantity of oxygen measures 1 litre at standard temperature. At what temperature will its volume be halved?

26. A certain volume of air measures 1 litre under 738 mm. and at 17°. What will be its volume under 769 mm. and at 34°?

27. A quantity of hydrogen measures 320 cc. under 750 mm. and at 20°. What will be its volume at S.T.P.?

28. Reduce the following gas volumes to S.T.P.: (*a*) 150 cc. at 380 mm. and 18°; (*b*) 279 cc. at 1520 mm. and 300°.

29. A certain quantity of oxygen measures 1 litre under standard conditions. What will be its volume at 20° and 725 mm.?

30. 1 litre of oxygen under standard conditions weighs 1.43 gr. What will be the weight of 1 litre at 35° and 790 mm.?

31. 1 litre of air under standard conditions weighs 1.29 grs. Under what pressure will 1 litre weigh 3 gr.?

CHAPTER VI

COMPOUNDS OF HYDROGEN AND OXYGEN. WATER. HYDROGEN PEROXIDE

History.—Water has always been known to man and has been a substance of the very highest importance to him. Hence, people who were given to speculating about things, have devoted a good deal of their mental energies to the subject of water, and many curious ideas have resulted.

According to the account given in Genesis, the Hebrews believed that water was one of the first things created. In ancient India and Egypt, it was held that water was the very first thing created and that everything else had been made from it, and certain of the Greek philosophers were of the same opinion. All through the Middle Ages, people talked of "the four elements of Aristotle," earth, air, fire, and water, and up to quite a late date, water was believed to be undecomposable. Cavendish showed, in 1781, that water is produced when hydrogen burns in oxygen; but he mixed up with this fact a peculiar theory which he held, and it remained for the great French chemist, Lavoisier, to clearly announce that water is nothing more or less than a compound of oxygen and hydrogen.

Occurrence.—This substance, as we all know, occurs to an enormous extent in nature, though never quite pure. It is found as a solid, ice, at all times in the polar regions and on the tops of high mountains, and during the winter in a great many other places. As liquid, water, it forms oceans, lakes, rivers, streams, etc., and also a large part of plants and animals — the human body is about $\frac{2}{3}$ water, and apples about $\frac{4}{5}$; and it is present to a greater or less extent in all soils and rocks. And as a gas, water-vapor, it is at all times present in the atmosphere.

Preparation.—Water may be prepared from its elements, as when hydrogen burns in oxygen or in air:

$$2H + O = H_2O,$$

but this is done only in exceptional cases, such as we shall meet with later in discussing its composition. It is usually obtained from natural sources, but as it is never found free from other substances, it must be purified. The impurities which it contains are of two kinds: (*a*) those held in suspension, like fine sand, clay, chips, etc., and (*b*) those held in solution like salt, lime, etc. The former can be removed by *filtration*, *i.e.*, making the water pass through porous substances such as blotting paper, porous stones, layers of sand, charcoal, etc., the pores of which are too small to allow the

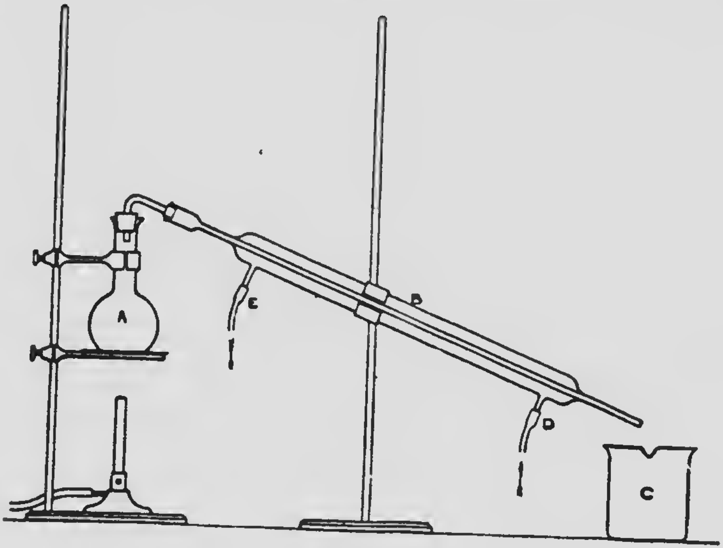

FIG. 11.

little solid particles suspended in the water to get through. (Many bacteria are too small to be filtered out.) The dissolved impurities (and suspended ones, too) can be removed by *distillation*, *i.e.*, by converting the water into steam (boiling), allowing the steam to travel away from the impurities and then condensing it into water again.

EXPERIMENT.—Arrange an apparatus as in the figure. *A* is the boiler, *B* is the condenser, and *C* the receiver. Connect the opening, *D*, by means of a rubber tube, with a tap or other supply of cold water, and *E* with a sink or other receptacle for overflow. Fill the flask *A* about one-third full with dirty water (or water colored with ink or litmus) and boil while a very slow stream of water runs through the condenser jacket. Distilled water will be obtained in the receiver.

When distillation is very carefully carried out, with a number of special precautions, pure water is the result.

Properties.—*Physical Properties.* Pure water is a liquid at ordinary temperatures, colorless in small quantities, but blue when seen in very thick layers; it is odorless and tasteless. If slowly cooled from its boiling-point, it contracts steadily till 4° is reached, after which it expands down to 0°, and then expands still more on freezing. This peculiar behaviour is of the utmost importance in nature, because if water contracted steadily as it cooled and also on solidifying, ice would form at the bottoms of streams, ponds, etc., and they would freeze solid during our winters. Water freezes at 0°, forming ice which, as has already been pointed out, is lighter than water, and it boils at 100°, forming steam. (A cubic inch of water forms nearly a cubic foot of steam.) The G.M.V. of steam (calculated, of course, to standard temperature and pressure) weighs 18 grams, therefore the molecular weight of steam is 18.

Water is capable of dissolving a larger number of substances than any other liquid—it is the best solvent known. The dissolved substances may be gases, such as oxygen;

liquids, such as alcohol; or solids, such as salt and sugar. It is no wonder, then, that water is not found pure in nature.

Chemical Properties.—Water is a compound which is not easily decomposed, or, as we say, it is very stable; it requires a very large quantity of heat, or some other form of energy, to separate its oxygen and hydrogen—indeed, the quantity of energy required to decompose a given quantity of water is exactly the same as the quantity of energy evolved (as heat) when enough oxygen and hydrogen combine to form this quantity of water. (This is true of all chemical compounds.)

A great many substances when deposited from solution in water, separate out in the form of regular solids called crystals, and the process of separation is called crystallisation from solution.

Experiment.—Half fill a bottle (holding about 500 cc.) with cold water. Add powdered alum in small quantities and shake well after each addition. Continue, until no more alum will dissolve and a little of the solid is left in the bottom of the bottle. Allow to stand until the liquid clears, and then carefully pour it off into a beaker. Heat almost to boiling and stir in more powdered alum until no more will dissolve easily. Pour the clear, hot solution into another beaker and allow it to cool slowly.

In the case of many of these substances, if the crystals be removed from the solution, carefully dried with blotting paper, and heated in a tube, they are found to give off a definite proportion of water which was chemically combined in them. Such water, chemically combined in crystals, is called **Water of Crystallisation.**

Experiment.—Dry some of the small alum crystals obtained in the preceding experiment by pressing them between blotting papers, and then place two or three grams of them in a dry test-tube. Hold the tube in an inclined position and heat just the bottom. What happens to the alum? What happens to the upper part of the walls of the test-tube? How do you explain this?

Repeat the experiment, using small crystals of copper sulphate (blue vitriol, blue stone) instead of the alum.

Some compounds, such as washing soda, containing water of crystallisation give it up simply on exposure to the air at ordinary temperatures; such substances are said to be **efflorescent.** (It must be carefully noticed that, in order to be termed efflorescent, the substance must give off water that has been in combination, *i.e.*, that has been water of crystallisation. The family washing, drying on the clothes-line, is not efflorescent.) Certain other compounds, like calcium chloride, are capable of absorbing moisture from the air, and they are termed **deliquescent.** (They do not necessarily convert the moisture into water of crystallisation, so a deliquescent substance cannot be correctly defined as "the opposite of an efflorescent substance.") Deliquescent substances are often used for drying gases, and the fact that they deliquesce in air proves that this gaseous substance contains water.

EXPERIMENT.—Place a little dry calcium chloride in a watch-glass and allow it to stand exposed to the air for some hours. What does the result teach with regard to calcium chloride? With regard to the air? The calcium chloride may be dried by heating and used over again.

Composition of Water.—If we wish to find out the composition of any compound, there are two general methods of attaining our end: we may start with the compound and break it up into its elements; or, we may start with the elements and build up the compound. These two methods are respectively analysis and synthesis, and these terms have already been defined (p. 25). If we are to do this work thoroughly, we must determine not only what elements go to make up the compound, but also how much of each. In other words—our experiments must be both qualitative and quantitative.

To determine the composition of water analytically, we make use of the experiment, already described, in which the water is decomposed by electrolysis, *i.e.*, by the help of an electric current (see p. 38). We may test the gases obtained, and thus discover the qualitative composition of the water; and we may also measure the gases and arrive at the quantitative composition.

We have already seen that water is formed [illegible] hydrogen burns in oxygen. [illegible] we [illegible] method for showing the composition of [illegible] qualitatively. To make [illegible] quantitative, the quantities of oxygen [illegible] hydrogen must be measured. A graduated glass [illegible] closed at one end, has two [illegible] wire fused through opposite [illegible] the closed end, and almost [illegible] the tube. Such a tube is called [illegible] eudiometer. The eudiometer is filled with mercury [illegible] in a mercury trough. Then oxygen is passed into it and the quantity measured [illegible] of the graduations on the [illegible] then [illegible] is passed in and [illegible] measured. [illegible] being taken, an electric spark is passed between the ends of the platinum wires, [illegible] and hydrogen [illegible] noiselessly. The [illegible] a minute drop of water, [illegible] if the oxygen and hydrogen [illegible] proportion of one volume of [illegible] no gas is now left in the eudiometer [illegible] any other proportions, the excess of one [illegible] the other [illegible] the case may be, will be left uncombined at the close of the experiment.

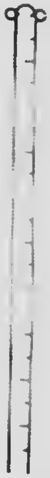

Fig. 12.

As the exact measurement of pure gases is very difficult to carry out, roundabout methods are often devised to avoid such measurements. Here is one connected with the synthetical proof of the composition of water. It is based [illegible] that [illegible], a compound of copper and oxygen, [illegible] oxygen when simply heated, if, however, while it is heated, hydrogen be passed over it, the "shaking" action of the heat and the affinity of the hydrogen for the oxygen are together too much for the copper oxide and it gives up just enough oxygen to produce water with the hydrogen, but no more (see experiment, p. 42). Hydrogen, then, is purified and passed through a tube containing a little porcelain boat filled with copper oxide, and kept hot. The products pass on through a tube containing calcium chloride, a deliquescent substance, which absorbs the water vapor formed. The calcium chloride tube [illegible] weighed before and after the experiment, the gain in weight being due to the water formed. (This gives H + O.) The boat with its copper oxide is also weighed before and after the experiment, the loss being due to the oxygen that combined [illegible] the hydrogen to form the water. (This gives O.) The difference between the gain in weight of the chloride [illegible] and the loss in weight of the copper oxide is the weight of hydrogen in the water formed:

$$(H + O) - O = H$$

(The equation, as here written, is to be regarded mathematically rather than chemically.)

All the best results that have been obtained by experiments such as those described above have been collected, and we find that they agree wonderfully closely—they are not all exactly alike, for no man can expect to get absolutely correct results—and, if we take the average of them, the composition of water turns out to be

	By Volume	By Wei	
Oxygen	1	88.814	or
Hydrogen	2	11.186	

For our present purpose it will be quite near eno that water is made up of 2 parts of hydrogen to 1 part of oxygen *by volume*; or 2 parts of hydrogen to 16 parts of oxygen *by weight*. The former is spoken of as the volumetric composition of water and the latter as the gravimetric. (In mentioning quantities, it is *very important* to state whether they are volumes or weights; unless this is done, weight is understood. Hence, to say "Water is made up of 2 parts of hydrogen to 1 part of oxygen," is incorrect.)

NOTE

Natural Waters.—Before leaving the subject of water, it will be well for us to take up a little applied chemistry, by discussing natural waters very briefly.

As we have already learned from our experiments, pure water is made up of oxygen and hydrogen in a certain definite proportion and nothing else; but the various kinds of water that we find in nature always contain more or less of something else, which is regarded as impurity. One of the things that the old alchemists vainly strove to prepare was "the universal solvent": that liquid which was to dissolve everything (and was to be kept in—what?) As is so often the case, we think that that which is far off, or rare, must be so much more important than that which is close at hand and common; and so, in this connection, the alchemists ignored water, which will dissolve a greater variety of things than anything else we know (and must therefore be very carefully kept in something special if it is to remain pure). Hence, we should hardly expect to find it pure in nature, where it comes into contact with such a variety of materials.

The purest natural water is rain water, collected after it has rained for some time and thus washed the air free from dust; it has been distilled by nature and has had an opportunity of absorbing impurities only from the air. As soon as it gets to the ground, however, it finds many soluble substances, and these it dissolves somewhat and carries along with it into springs, streams, rivers and finally to the sea. Waters containing a good deal of such material in solution are called mineral waters (sea water is really a mineral water), while those containing only a very little are called fresh waters. The proportion of solid matters in solution in a given water may be determined by carefully evaporating to dryness a weighed quantity of the water and weighing the residue.

EXPERIMENT.—Weigh carefully a clean, dry porcelain dish of about 500 cc. capacity and measure into it 300 cc. of some kind of mineral or hard water. (300 cc. of water weighs 300 gr.) Place the dish on the top of a beaker containing some water and boil this water. Gradually the water in the dish will evaporate, without sputtering and loss of material, and the operation is continued (putting more water into the beaker, if necessary) till the contents of the dish are quite dry. Weigh the dish and its contents, and calculate the number of parts of solid matter per thousand of water.

The following table will give some idea of the quantities we are dealing with here, the figures being averages of a great many experiments such as the one just described.

SOURCE OF WATER	TOTAL SOLIDS IN 1,000 PARTS OF THE WATER
Rain Water	0.03
Rivers and Lakes	0.10
Deep Wells	0.44
Mid Atlantic	35.98
Dead Sea	228.57

Natural waters also contain gases in solution, principally air and carbon dioxide, which separate out in the form of little bubbles when the water is heated, and before it boils.

As one of the principal uses of water is for drinking purposes, it is often a matter of great importance to be able to find out whether water from a certain source is wholesome or not (potable, drinkable). This cannot generally be accomplished by chemical means, though valuable hints can often be obtained in this way. The dangerous impurities in drinking water are disease germs which have generally been introduced in sewage, and their presence (or absence) should be determined by a proper bacteriological examination which is quite beyond the scope of chemistry. In all cases where water may be infected with disease germs, it should be thoroughly boiled before being drunk—this kills the germs (boiled eggs will not hatch). For city use, water is often filtered through sand-beds, whereby the suspended matter is strained out, and many of the dangerous bacteria are actually eaten up by harmless bacteria that live in the sand-beds. Water is often distilled for industrial purposes, large boilers being used and the steam being condensed in spiral metal pipes, called worms, sometimes made of pure tin and surrounded by a current of water to keep them cool. This, of course, removes all impurities. Hard waters, which we shall consider later on in connection with lime, are very troublesome for steam boilers and in washing. They are often softened by adding certain chemicals in proper quantities.

Nature, if given time enough, will generally purify contaminated water herself, as far as suspended impurities, including bacteria, are concerned. Sand, clay, etc., are slowly deposited when the water is still enough for a sufficient length of time; and the oxygen dissolved from the air brings about a slow combustion (destruction) of the bacteria, and other animal and vegetable impurities.

The oxygen which exists *in solution* in water mus[illegible]ully distinguished from that which exists *in combination*. We may pu[illegible] of wood together into the form of a box, by means of nails. When the bo[illegible]s finished, we might throw in a lot of nails and use it as a nail-box in the work-shop. If we should take out all the nails thrown in, we should say the box was empty of nails, although there were some left in its construction. It is only those loose nails in the box—not in its construction—that can be used for other purposes. Dissolved oxygen in water is like the nails thrown into the box and useful for other purposes: combined oxygen in water is like the nails used in the construction of the box, and not useful for other purposes, except in very unusual cases.

Hydrogen Peroxide.—As we have seen, water is made up of hydrogen and oxygen combined in the proportions of 2 parts by weight of hydrogen to 16 parts of oxygen. A second compound of these two elements is known, hydrogen peroxide, or hydrogen dioxide, which contains 2 parts by weight of hydrogen to 32 parts of oxygen. This compound (which is prepared by treating a solid substance called barium dioxide with sulphuric acid:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2)$$

is a colorless, odorless liquid, which breaks down very easily into water and oxygen:

$$H_2O_2 = H_2O + O$$

When the hydrogen peroxide is pure (*i.e.*, not dissolved in water), this decomposition is liable to take place so rapidly as to cause an explosion. The hydrogen peroxide sold by druggists is a water solution containing 3% of H_2O_2. It is used in medicine as an antiseptic, its capacity for killing germs being due to the oxygen which it gives up so easily, and which oxidises the germs, the oxygen being in the nascent state (see p. 89). This solution is most valuable in the household for cleaning out cuts, scratches, etc., thus preventing festering. It is also a valuable mouth-wash. Hydrogen peroxide, because it so easily gives up oxygen, is also a valuable bleaching agent, being used for bleaching many delicate fabrics and also human hair, producing in this last case a sort of straw color which is considered fashionable by some persons.

If a little powdered manganese dioxide be added to a solution of hydrogen peroxide, all this last is immediately decomposed, the oxygen being given off. This method is used in analysing it, the oxygen being collected and measured. This action of manganese dioxide is particularly interesting, because it is so very like the effect it has on fused potassium chlorate, making it give up its oxygen. It is a catalytic agent.

QUESTIONS

1. 15 cc. pure oxygen is added to 20 cc. pure hydrogen in a eudiometer over mercury. A spark is passed through the mixture. Will any gas be left uncombined? If so, what will it be, what will it measure? Why did it not all combine?

2. How could you show that spring water is really a dilute solution of some solid?

3. What importance is to be attributed to the fact that the maximum density of water is some degrees above its freezing point?

4. Does the fact that ice is less dense than water have any particular significance in nature?

5. What is the source of the moisture that collects on the chimney of a newly lighted lamp? Where does it go to?

6. Make a diagram of the apparatus employed in distilling water, explaining the action of each part.

7. Into what two classes can the methods for determining the composition of water be divided?

8. What is the difference between qualitative and quantitative analysis?

9. In determining the quantitative composition of water by passing hydrogen over a heated oxide, could HgO be substituted for CuO? Why?

10. How might drinking water be obtained from sea water?

11. Does hot water dissolve more than cold water (*a*) in the case of gases; (*b*) in the case of solids? Do you think that one of these principles has any bearing on the little bubbles that form when water is slightly warmed, and on the flat taste of water that has been boiled and cooled?

12. Which is the purer, filtered water or distilled water? Why?

13. How could one determine the proportion of solid matter dissolved in spring water? Describe in detail the apparatus you would use and the method of using it.

14. How might the proportion of water in an apple be determined?

15. Give two reasons for using metal rather than glass tubes in distilling water on the large scale.

16. In one of Duma's experiments to ascertain the composition of water, by passing hydrogen over heated copper oxide, the following results were obtained :

Wt. of cupric oxide and tube before experiment	334.598 gr.
Wt. of cupric oxide and tube after experiment	314.236 gr.
Wt. of drying tubes before experiment	426.358 gr.
Wt. of drying tubes after experiment	449.263 gr.

Calculate from these the percentage composition of water.

17. What is the difference between filtration and distillation? Describe each, mentioning the kinds of impurities separated.

18. When 2 gr. of hydrogen combine with 16 gr. of oxygen to form 18 gr. of water, a quantity of heat equivalent to 68,400 calories is given off. How many calories would be required to decompose 18 gr. of water ?

19. How much water is there in a ton of gypsum, $CaSO_4 . 2H_2O$?

20. Describe a eudiometer, with a figure. Describe one without a figure and ask yourself whether your descriptions could be misunderstood by a person who does not know what a eudiometer is.

CHAPTER VII

THE LAWS OF COMBINING PROPORTIONS AND THE ATOMIC THEORY

Thousands and thousands of determinations of the composition of water have been made by hundreds of different chemists, and the results all go to show that the hydrogen and oxygen that form the water are always combined in exactly the same proportions. Precisely the same sort of thing has always been found to be true in the case of every other compound that has been examined. Hence, we may formulate a general statement:

The Law of Definite Proportions.—*Substances combine in definite proportions to form compounds* (or, a compound always consists of the same elements combined in exactly the same proportions).

Thus, in the case of water, as has already been pointed out, the proportion of oxygen to hydrogen is always exactly the same, no matter where the water comes from or how the determination is made.

But, although we find that hydrogen and oxygen always combine in exactly the same proportions to form water, *i.e.*, 2 of hydrogen to 16 of oxygen, by weight, we have seen that they combine in another proportion to form hydrogen peroxide, *i.e.*, 2 of hydrogen to 32 of oxygen. This latter compound always contains the hydrogen and oxygen in exactly these proportions, and thus it too comes under the law of definite proportions. If we examine the proportions in hydrogen peroxide and then the proportions in water, we are at once struck by the fact that the 32 of oxygen which combines with the 2 of hydrogen in one case is exactly double the 16 that combines with the 2 in the other case. Here, again, a further study of a large number of cases shows that we are dealing with one of the great uniformities of nature, and we are again able to enunciate a law.

Law of Multiple Proportions.—*When two substances,* A *and* B, *combine to form more than one compound, then the different quantities of* B, *that unite with any fixed quantity of* A, *bear a very simple ratio to one another, i.e.*, the ratio of small whole numbers.

In the case of water and hydrogen peroxide, for instance, we have

	WATER	HYDROGEN PEROXIDE
Hydrogen (A)	2	2
Oxygen (B)	16	32

the ratio of the two quantities of B (oxygen) being 16 : 32, *i.e.*, 1 : 2.

The two laws just enunciated are known as **Laws of Combining Proportions.** The composition of every chemical compound is an illustration of the law of definite proportions, and we shall find many examples of the law of multiple proportions as we proceed.

The general outline of part of the scientific method as employed in the chapter on the molecular theory was

Observation :	All Facts
Classification :	Classes of Facts
Generalisation :	Law
Speculation	Theory
Deduction :	Molecular Weights

We are now considering the class of facts concerning the proportions in which chemical substances combine, and we have discovered that all the relations may be grouped under two great generalisations, or laws. Immediately the old longing for a reason asserts itself. We have observed (from the point of view of proportions) *how* things combine—now, *why* do they do it? Here, again, comes in the scientific use of the trained imagination. John Dalton, an English schoolmaster, who made a number of valuable physical and chemical discoveries—among them being the law of multiple proportions—propounded, in 1807, a theory to account for these laws, which may be enunciated as follows:

Atomic Theory.—*The elements are made up of indivisible particles, called atoms. It is between these atoms that chemical combination takes place.*

Let us consider these two statements a little more carefully. And first: the very kernel of this theory is the *indivisibility* of the atoms; as we shall see in a moment. The word itself should constantly remind us of this, because it is derived from two Greek roots, *a*, un-, and *tom*, cuttable, *i.e.*, uncuttable. Further, the atoms must be extremely small; and further still, as all samples of any element, oxygen, for instance, always exhibit the same properties (under the same conditions), we must conclude that all the atoms of the same element are alike, particularly in weight.

Those who have followed the work done in recent years in connection with radium, will know that many physical chemists believe that they have evidence there of the disintegration of atoms, and that therefore an atom is not indivisible. It should, however, be remembered that the atomic theory postulates indivisibility only as far as ordinary chemical reactions are concerned—not in radioactive changes. The atomic theory is still as "true" and useful to the chemist as it ever was.

Secondly, these atoms are the things that are responsible for chemical combination. Just as, when we read that in a certain town four hundred people were married last year, we know it means that *each one* of two hundred women was married to *each one* of two hundred men by an individual ceremony, and not that a crowd of two hundred women were married all at one time and collectively to two hundred men, each woman being married to $\frac{1}{200}$ of each man; so, in chemical combination, a large mass of one substance does not combine bodily with a large mass of the other, but the separate atoms of the one combine with the separate atoms of the other. (Similarly, when men in a factory are paid, each man receives his individual wage; and, when marks are allotted in an examination, each candidate receives his own due—the aggregate of marks is not presented to all the candidates in a mass.)

An Atom may be defined as *the smallest quantity of an element that can enter into chemical combination.* (There is, of course, no such thing as the atom of a compound.)

In the simplest case of combination, one atom of one substance will combine with one atom of the other to form the smallest possible part, the molecule, of the compound. Such is the case with the iron and sulphur of the experiment on p. 24. One atom of iron unites with one atom of sulphur to form one molecule of iron sulphide. As iron sulphide, to be iron sulphide, must contain both iron and sulphur, this is the smallest possible quantity that can exist, because we cannot cut an atom, and hence cannot get less iron and less sulphur to form a smaller quantity.

The molecule of iron sulphide, then, consists of iron and sulphur combined in the proportions of the weights of their respective atoms, which, as we shall learn later, are 56 and 32. Any *mass* of iron sulphide is made up of such molecules, and therefore in it the iron and the sulphur must be present in the exact proportions in which they are present in each *molecule*, *i.e.*, 56 : 32. The same sort of thing would be true in the case of more complex molecules. In water, for instance, one atom of oxygen, weighing 16, is combined with two atoms of hydrogen, each weighing 1, to form the molecule of water, weighing 18; each molecule contains oxygen and hydrogen in the proportion of 16 : 2, and any number of water molecules must contain them in the same proportions; hence, water must always contain oxygen and hydrogen in exactly these proportions. But this is just the sort of thing the law of definite proportions says of all compounds. Therefore, the atomic theory explains, or accounts for, the law of definite proportions. Or, to put it differently, if the atomic theory represents the truth, then the law of definite proportions follows as a necessary consequence.

We find, however, that although iron and sulphur always combine in the same proportions to form iron sulphide, there is another compound of these elements which contains more sulphur than the one we have already been discussing (pyrite, FeS_2). If, in accordance with our theory, the first compound contains one atom of sulphur to each atom of iron, and we wish to prepare another compound with more sulphur, we must add another whole atom (or two, or three); and therefore the quantity of sulphur in the new compound will bear a very simple ratio to the quantity in the old, *i.e.*, twice as much (or three, or four times as much). This, however, is the law of multiple proportions, appearing as another necessary consequence of our atomic theory. The water molecule contains 2 atoms of hydrogen combined with 1 of oxygen; the hydrogen peroxide molecule, 2 atoms of hydrogen combined with 2 atoms of oxygen—another example of this same law.

Inasmuch as the atomic theory considers that all chemical changes consist in rearrangements of atoms, the weights of these suffering no alteration during the changes, the theory explains the law of conservation of mass as well as the laws of combining proportions.

We have spoken above about the weights of atoms. These particles are so extremely small that it is absolutely impossible to weigh one of them. (It has been calculated that 1 hydrogen atom weighs 0.000,000,000,000,000,000,000,000,14 gr.) But, as will be shown, we can determine their relative weights. We must then choose one as a standard and refer all the others to it. The original choice was hydrogen = 1, now it is oxygen = 16; the difference between the two is, however, so very small (O : H :: 16 : 1.008) that we need not consider it here, especially as we are not carrying our discussion out to several places of decimals.

Let us suppose that we wish to determine the atomic weight of oxygen (on the standard H = 1). We know of a number of substances containing oxygen, whose molecular weights we can determine, *i.e.*, we can find out the weights of a number of different molecules containing oxygen; and, by analysing the compounds, we can find out what proportion of each one of these molecules is oxygen. Now, it is more than likely, it is practically certain, that at least some of these molecules will contain only *one* atom of oxygen. Hence, if we choose the smallest quantity of oxygen ever found in one molecule (of anything containing it), we may be pretty certain that this is one atom.

SUBSTANCE	WEIGHT OF 22.4 LITRES, IN GRS.	O	OTHER ELEMENTS
Water (steam)	18	16	Hydrogen, 2
Carbon monoxide	28	16	Carbon, 12
Oxygen	32	32	
Carbon dioxide	44	32	Carbon, 12
Sulphuric anhydride. . .	80	48	Sulphur, 32

None of these molecules contain less than 16 parts by weight of oxygen, hence we assume this to be the weight of one atom, *i.e.*, its atomic weight. We are supported in this by the fact that all the other quantities of oxygen occurring in molecules, are whole-number multiples of 16, *i.e.*, the other molecules contain 2, 3, atoms of oxygen.

There are many other, indirect, methods for determining atomic weights, but they cannot be discussed here.

The Atomic Weight *of an element is the smallest weight of the element ever found in a molecule.*

In the table given above, we notice one very striking thing, *i.e.*, that the molecular weight of oxygen itself is twice its atomic weight. There are other facts, however, which tend to show that this must be true. If we perform the experiment described on page 60, at a temperature above 100°, so that the water produced will remain in the form of steam, we get the following result :—

1 vol. O + 2 vols. H = 2 vols. steam.

If we apply Avogadro's hypothesis, we get

x mol. O + 2x mol. H = 2x mol. steam

and dividing through by x gives us

1 mol. O + 2 mols. H = 2 mols. steam.

Now, each molecule of steam (water) must contain some oxygen. Hence, the molecule of oxygen that we started with has been split into two parts, one being in each molecule of the steam. Therefore, as an atom is indivisible, a molecule of oxygen must contain at least two atoms, so as to be divisible into two parts. We have, up to the present time, no reason for believing that it contains *more* than two atoms; hence, we accept the result given in the table above, *i.e.*, that two atoms are contained in the molecule of oxygen. (We may picture the thing to ourselves thus: oxygen atoms desire to combine; if they can't get anything else to combine with, they will form pairs with one another.) The same sort of thing has been found to be true of hydrogen, *i.e.*, its molecule contains 2 atoms. This is the reason why hydrogen = 2 (not = 1) is selected as the standard for molecular weights.

(NOTE.—The particles postulated in the molecular theory are *separate*, or discrete, those postulated in the atomic theory are *indivisible*. Further, we have atoms of elements only; but molecules of both elements and compounds.)

A table of the elements with their symbols and atomic weights will be found on page 263.

QUESTIONS

1. Mention three compounds that illustrate the law of definite proportions. Tell why you think they illustrate it.

2. Enunciate the law of multiple proportions. Show how water and hydrogen peroxide illustrate this law, *without using their formulas in your answer, or making any reference to atoms.*

3. For what purpose was the atomic theory formulated?

4. Criticise the following enunciation of the atomic theory: Substances are made up of infinitely small particles called atoms, between which chemical combination takes place.

5. Why do we think that all the atoms of any one element are alike? That they are extremely small?

6. Upon what laws is the atomic theory based? and how does it account for these laws?

7. Define the term atom and tell how atomic weights are determined.

8. Why do we think that the molecule of oxygen contains two atoms?

9. Why was hydrogen chosen as unit substance for atomic weights? Would there be any objection to using O = 1?

10. What surprising conception of matter is introduced by the atomic theory?

11. What is the difference between an atom and a molecule? Are the two ever the same? (See argon.)

12. Can you find any fault with the expression "Avogadro's law"? Why?

CHAPTER VIII

SYMBOLS, FORMULAS, EQUATIONS, CALCULATIONS

Everybody knows that, in writing, we constantly make use of a large number of contractions and signs, such as Mr. for Mister and St. for street, + for plus and $ for dollars. In chemistry, too, it has been found that a great deal of time can be saved and a great many things more clearly expressed by employing suitable symbols, etc.—a sort of chemical shorthand.

Instead of writing out the name of an element in full, we make use of its initial letter, or letters (sometimes of its Latin name), and this is called the symbol of the element. Furthermore, it is agreed among chemists that this symbol shall represent a definite quantity of the element, *i.e.*, one atom. We thus have the following definition:

A Symbol *is a capital letter, or a pair of letters, one capital and the other small, that stands for one atom (of an element).*

Thus, O stands for one atom of oxygen, H for one atom of hydrogen, Fe for one atom of iron (ferrum), and so on.

A few of the commoner elements, with their symbols and atomic weights, are given in the following table:

Bromine	Br	80	Mercury	Hg	200
Calcium	Ca	40	Nitrogen	N	14
Carbon	C	12	Oxygen	O	16
Chlorine	Cl	35.5	Phosphorus	P	31
Fluorine	F	19	Potassium	K	39
Hydrogen	H	1	Silicon	Si	28
Iodine	I	127	Sodium	Na	23
Iron	Fe	56	Sulphur	S	32
Magnesium	Mg	24	Zinc	Zn	65

The atomic weights given in the preceding table are, in some cases, only approximate, but are quite near enough for all ordinary purposes, including calculations. A more extensive list of the elements will be found on page 263.

When atoms have combined to form molecules, we represent this by writing the proper symbols side by side. This we call a formula, which we may define thus :—

A Formula *is made up of symbols, written side by side, and stands for one molecule (of an element or compound).*

Thus, FeS is iron sulphide, H_2O, water, etc. Small numbers written a little below the line multiply the symbol immediately preceding and indicate combination; thus, H_2O means HHO, H_2SO_4 means HHSOOOO. A number on the line multiplies the symbol or whole group that follows, but does not indicate combination; thus, $2H_2O$ is the same as $2(H_2O)$, *i.e.*, HHO + HHO (not HHOHHO), that is, two independent molecules of water, and $3N_2O_3$ means NNOOO + NNOOO + NNOOO. O is the symbol for oxygen, O_2 is its formula, *i.e.*, two atoms combined together, and O_3 is the formula for ozone.

Elements	. Atoms	. Symbols
Elements and Compounds . . .	. Molecules . . .	. Formulas

It should be carefully remembered that symbols and formulas have both qualitative and quantitative significance; that is, they not only indicate certain kinds of matter, but also definite quantities of these kinds.

The determination of the formula of a substance is an exceedingly important thing in chemistry, because, as we shall see as we proceed, the knowledge of a correct formula is useful in a very large number of ways, and saves a great deal of time and mental energy. Let us suppose then, as an example, that we wish to determine the formula of water, *i.e.*, the expression which represents one molecule of this substance.

First, we determine by experiment what elements are present—we analyse the substance qualitatively; and, from the result, the formula must be OH, or HO_2, or O_3H_5, or something of that sort; briefly, H_xO_y

Second, we determine the proportions in which the constituents are present, we analyse the substance quantitatively, and get

Hydrogen	11.2%
Oxygen	88.8%

Third, we reduce the percentage proportions to atomic-weight proportions (sometimes called atomic ratio). We think it out thus: the atomic weight of hydrogen being 1, 11.2 parts represents (mathematically) 11.2 atoms; and the atomic weight of oxygen being 16, 88.8 parts represents $\left(\frac{88.8}{16}\right)$, 5.5 atoms. Hence, the ratio of the atoms of hydrogen to oxygen is 11.2 : 5.5. Now, atoms are indivisible; we cannot have fractions, so we must choose whole numbers—and preferably small ones—that will represent the ratio thus obtained. Evidently 2 : 1 will do. Hence the formula of water may be H_2O. Of course, H_4O_2 or H_6O_3 will do just as well as far as quantitative composition goes, but these formulas represent molecules of very different sizes—one must be correct and the others wrong. Hence, the next step.

Fourth, we determine the molecular weight of the substance, *i.e.*, we find out how much 22.4 litres of it, in the state of gas, would weigh in grams under standard conditions. Of course, we cannot actually weigh steam at zero, it would condense; neither is it likely to be convenient to weigh exactly 22.4 litres. But we weigh any *known volume*, under any *known* conditions and then, *by calculation*, find out what 22.4 litres of steam would weigh under standard conditions if it did not condense. This turns out to be 18 grams. Hence, 18 is the molecular weight of steam and our formula must represent this. H_2O does, because $2+16=18$; H_4O_2, H_6O_3, do not. Hence, H_2O represents the molecule of steam and is therefore called the formula of water. It may of course be written OH_2 or HOH, if desired.

Outline of method for determining a formula:

1. Qualitative analysis.
2. Quantitative analysis.
3. Atomic ratio.
4. Molecular weight.

As has already been pointed out, we must not expect absolute mathematical accuracy in the numbers obtained, first, because our analyses, etc., can never be absolutely correct, and, second, because we do not wish to complicate matters here by carrying out calculations to a great many decimal places.

Having once determined a formula, we file it away, as we file away addresses in an address-book, and whenever we want any of the numbers that went to produce it, we can calculate them backwards from the formula and so reproduce them. A few formulas we commit to memory, just as we remember a few addresses that we need to use often. What a mental saving is effected in this way! It is easy to commit to memory

H_2O is water
$H=1,\ O=16$

from which we can very easily deduce a number of other quantities. How much more difficult it would be to try to remember

> Water is composed of hydrogen and oxygen in the proportion of 11.2 to 88.8. 22.4 litres at standard temperature and pressure weigh 18 grams, etc.

It must, however, always be remembered that facts are the primary things, formulas only convenient records of facts.

The choice of a symbol is a purely arbitrary one; thus, for iron, we might choose I or Ir or Fe or F. As long as all chemists agree, it does not matter much which is chosen. But, as soon as symbols have been decided upon, the choice of formulas is not at all arbitrary; an actual appeal to facts must be made, and the results determine the formula absolutely.

Just as we can represent substances by symbols and formulas, so we can represent reactions by equations.

A Chemical Equation *is an equation made up of symbols and formulas and represents a chemical reaction*, as determined by experiment.

Thus, when mercury, Hg, is heated in air or oxygen, it combines with oxygen to form the compound mercuric oxide; moreover, it has been found by quantitative experiment that 200 parts by weight of mercury combine with 16 parts by weight of oxygen. These happen to be the atomic weights of the elements, therefore the reaction is represented thus:

$$Hg + O = HgO$$

When oxygen and hydrogen combine, the proportions by weight are 16 : 2; to represent this by symbols we must use 2H, as each H weighs only 1; therefore, we write

$$O + 2H = H_2O$$

The meaning of the equations already given in the text will now be clear.

It must be carefully remembered that equations have been devised to represent reactions that have been studied out both qualitatively and quantitatively: the reaction existed first and the equation is meant to be a sort of picture or record of it. Just because an equation is correct algebraically, is not proof that it represents a real reaction. Thus, we might write

$$2KClO_3 = 2K + 2ClO_2 + O_2,$$

an equation which "balances" all right; but, although all the formulas used in it represent real substances, no such reaction is known, and there are a great many reasons for believing it impossible. Whether an equation that balances really represents an actual chemical change, or not, can be determined only by experiment. Of course, if an equation does not balance, it indicates creation or destruction of matter, and therefore must be wrong.

Equations then are to be regarded as accurate records of careful observation of reactions. As such they furnish valuable data for chemical calculations. In this connection, it must be carefully kept in mind that *the proportions which they directly represent are weights and not volumes.* We should remember, however, that a quantity *of any gas,* equal to its molecular weight expressed in grams, occupies 22.4 litres. Hence, as O_2 is the molecule of oxygen,

$$\begin{array}{ccccc} HgO & = & Hg & + & O \\ 216 & & 200 & & 16 \end{array}$$

216 grams of HgO produces 11.2 litres of O ; and

$$\begin{array}{ccccc} KClO_3 & = & KCl & + & 3O \\ 122.5 & & 74 & & 48 \end{array}$$

122.5 grams of $KClO_3$ produces 33.6 litres of O. Further

$$\begin{array}{ccccc} 2H & + & O & = & H_2O \\ 2 & & 16 & & 18 \end{array}$$

22.4 litres of H + 11.2 litres of O produce 22.4 litres of steam; and

$$CO + O = CO_2$$

22.4 litres of CO + 11.2 litres of O produce 22.4 litres of CO_2

Suppose, for instance, that we wish to find out how much oxygen can be obtained from 500 grs. of mercuric oxide. The first question we would ask ourselves is: Do we know *any* quantitative relation between mercuric oxide and oxygen? Why, yes—there's that equation :

$$\begin{array}{l} HgO = Hg + O \\ 216 \;\; = 200 + 16 \end{array}$$

which tells us, as indicated by the numbers, that 216 parts of HgO give 16 of oxygen; hence,

$$1 \text{ part of HgO gives } \tfrac{16}{216} \text{ of O};$$

$$\text{hence, 500 gr. of HgO gives } \tfrac{16}{216} \times 500 \text{ gr. O}$$

If we want to know what the volume of this oxygen is, we recollect that 32 gr. of oxygen measures 22.4 litres; therefore, $\frac{16}{216} \times 500$ gr. oxygen will measure $\frac{16}{216} \times \frac{500}{32} \times 22.4$ litres.

Calculations involving weights only (no volumes) are *generally* the simplest; those involving volumes under standard conditions come next; while those involving volumes under other conditions are more complicated still. Hence, if we get a calculation of the second or third kind, we first convert it into one of the first, the general outline for all such calculations being:

(*a*) Reduce volumes to standard conditions.

(*b*) Reduce volumes at standard conditions to weights.

(*c*) Write equation representing the reaction involved.

(*d*) Put in atomic and molecular weights needed.

(*e*) Carry out proportion, or apply the unitary method.

(*f*) Convert weights thus obtained to volumes under standard conditions.

(*g*) Convert volumes under standard conditions to volumes under other conditions.

Of course some of the steps mentioned above are unnecessary in most examples. A couple of examples will make the method clear.

1. How much mercuric oxide could be obtained from 500 litres of oxygen at 18° and 735 mm., sufficient mercury being supplied?

(*a*) $$\text{Vol.} = 500 \times \frac{735}{760} \times \frac{273}{291} = 453.7 \text{ litres}$$

(*b*) $$453.7 \times \frac{1}{22.4} \times 32 = \mathbf{648.2\ gr.}$$

(*c*) $$Hg + O = HgO$$

(*d*) $$200 + 16 = 216$$

(*e*) $$1 = \frac{216}{16}$$
$$648.2 = \frac{216}{16} \times 648.2 \text{ gr.} = 8750 \text{ gr.}$$

(*f*) Not needed here

(*g*) Not needed here

2. What volume of oxygen at 15° and 740 mm. can be obtained from 327 gr. of potassium chlorate?

(*a*), (*b*) What weight of oxygen . . .

(*c*) $$KClO_3 = KCl + 3O$$

(*d*) $$122.5 = \ldots\ldots 48$$

(*e*) $$1 = \ldots\ldots \frac{48}{122.5}$$
$$327 = \ldots\ldots \frac{48}{122.5} \times 327$$

(*f*) $$\left(\frac{48}{122.5} \times 327\right) \times \frac{22.4}{32}$$

(*g*) $$\left(\frac{48}{122.5} \times 327\right) \times \frac{22.4}{32} \times \frac{760}{740} \times \frac{288}{273} = 97.2 \text{ litres}$$

QUESTIONS

1. Give some examples, other than those mentioned in the text, of symbols used in everyday writing.

2. Is O a symbol or a formula? What about O, O_2, O_3?

3. Give the meaning of each symbol and figure in the following expressions: H, Na, $2H_2O$, H_2SO_4, $CaSO_4\ 2H_2O$.

4. Calculate the percentage composition of CO and CO_2. Do you think that the numbers thus obtained suggest the law of multiple proportions?

5. Calculate the simplest formulas for the compounds which, on analysis, yield the following percentage results: (*a*) Mercury, 92.6;

Oxygen, 7.4. (*b*) Calcium, 29.5; sulphur, 23.5; oxygen, 47. (*c*) Carbon, 52.1; hydrogen, 13.1; oxygen, 34.8. (It must be remembered that results will not come out *exactly* in whole numbers, as these percentages are given to only one place of decimals.)

6. What is the symbol for oxygen? What is its formula?

7. What is the difference between the atom and the molecule of oxygen?

8. Define the chemical terms: symbol, formula, equation.

9. How is a symbol determined? What are the steps in determining a formula? Illustrate by an example.

10. 2.3 litres of steam at 113° and 775 mm. weigh 1.33 gr. Calculate the molecular weight of steam.

11. Tell [illegible] that the expression H_2O is meant to indicate.

12. Write two equations to represent each of the following classes of reactions: (*a*) analysis, (*b*) synthesis, (*c*) metathesis, (*d*) replacement. Define each of these terms.

13. Two compounds give on analysis the following: (*a*) oxygen, 53.25%, nitrogen, 46.75%; and (*b*) oxygen, 69.49%, nitrogen, 30.51%. Show that these compounds illustrate the law of multiple proportions.

NOTE.—*Other calculations will be found among the questions at the end of Chapters II and IV, and also in chapters succeeding this one.*

CHAPTER IX

CHLORINE AND ITS COMPOUNDS BROMINE — IODINE — FLUORINE

CHLORINE

History.—Karl Wilhelm Scheele, a wonderfully high-spirited Swede, shares with Priestley the honor of discovering oxygen; he made the discovery a little before Priestley but did not publish it till afterwards, and hence, according to scientific usage, the priority goes to Priestley. Scheele, however, does not need the credit of this discovery, as he made so many others, among them, in 1774, being that of chlorine, which he called "dephlogisticated marine acid air." For a long time chlorine was thought to be a compound (containing oxygen), but in 1810 the English chemist, Sir Humphrey Davy, showed that it was an element.

Occurrence.—This substance does not occur free in nature. When we come to study its properties and find out what an active substance it is, we shall not be surprised that, outside the laboratory, it is always found in combination. Its commonest compound, and the one from which it is always manufactured, is sodium chloride, NaCl, common salt; and, when we remember what an enormous quantity of salt there is in the oceans, in salt springs, and in the solid form of rock salt, we see that chlorine, in combination, occurs in pretty large quantities. Small quantities of it are found in combination with elements other than sodium, such as potassium, magnesium and silver.

Preparation.—As has already been indicated, the usual source of all chlorine is common salt, but there are various methods by which the element is obtained in the free state from this source. In one set of methods, the salt is treated with sulphuric acid and the mixture heated, when the following reaction takes place :

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

HCl is hydrochloric acid and this reaction is one of the steps in preparing soda from salt by the Leblanc process (see p. 197), the hydrochloric acid being a by-product. In order to prepare chlorine from HCl, *i.e.*, in order to tear away the H, we naturally cast about for some substance that the H would rather have than Cl, and we recollect its strong affinity for oxygen. The laboratory method consists in bringing HCl and MnO_2, manganese dioxide, together and warming the mixture.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl$$

Sometimes the MnO_2 and salt are mixed together and sulphuric acid added, when the following reactions take place :

$$\begin{array}{rrl}
2NaCl + & H_2SO_4 & = Na_2SO_4 + 2HCl \\
MnO_2 + & H_2SO_4 & = MnSO_4 + H_2O + O \\
2HCl + & O & = H_2O \quad + 2Cl \\
\hline
\multicolumn{3}{r}{2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + 2Cl}
\end{array}$$

EXPERIMENT.—*As chlorine has a very injurious effect on the throat and lungs, experiments with it should be carried on only where there is a good draught and care should be taken not to inhale the gas.*

Fit up a flask as in the figure, being sure that the thistle-tube reaches to within an eighth of an inch of the bottom of the flask. Put into the flask about 50 gr. of manganese dioxide (preferably in lumps about the size of peas) and pour in enough concentrated hydrochloric acid to cover it. Warm gently and chlorine will be evolved. The speed with which the gas is given off can be controlled by regulating the heating. As chlorine is soluble in water it cannot be collected over the pneumatic trough (it also attacks mercury); hence, as it is heavier than air, it is introduced into the bottoms of vessels in which it is desired to collect it and the air is lifted out. Of course, there will be some diffusion and the chlorine will not be quite pure. This method is called collecting by *downward displacement.* (When water is poured into a pail, it is collected by downward displacement.) Collect several cylinders of the gas and cover each with a piece of glass.

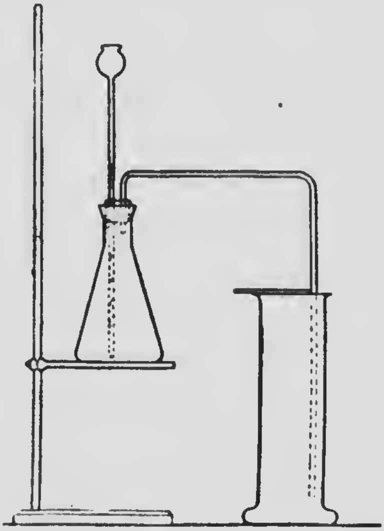

FIG. 13.

Properties. — Chlorine is a greenish-yellow gas, the name being derived from the Greek *chloros,* meaning greenish-yellow. It has a peculiar suffocating odor and, when breathed pure, produces a violent effect on the throat and lungs and may cause death; even in diluted form and in small quantities it produces effects very like a bad cold in the head. It is about two and one half times as heavy as air and 35.5 times as heavy as hydrogen, the G.M.V. weighing 71 grs. (What is the weight of the G.M.V. of air and of hydrogen?) It is soluble in water, one volume of the latter, under ordinary conditions, dissolving about three volumes of chlorine. Like all gases, it may be liquefied by cold and pressure, and this is comparatively easily accomplished in this case, only about six atmospheres being required at ordinary temperatures.

The smallest quantity of chlorine ever found in the G.M.V. of any gaseous compound containing it is 35.5 grams; hence, its atomic weight is 35.5.

Chlorine does not combine with oxygen under any ordinary conditions, but it has a strong affinity for hydrogen. A jet of burning hydrogen will continue to burn if passed into a jar of chlorine, hydrochloric acid, HCl, being produced, the two

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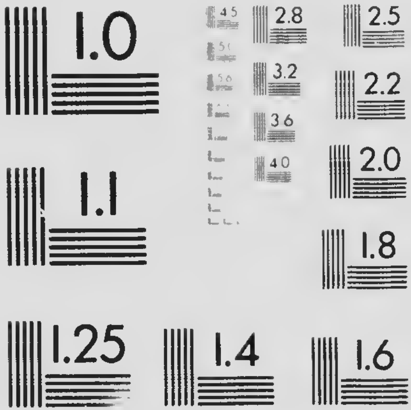
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gases combining in equal volumes. If a mixture of hydrogen and chlorine be prepared, it may be kept indefinitely in the dark; but combination takes place slowly in diffused daylight, and with explosive violence in strong light such as sunlight or that from burning magnesium (flash-light). Indeed, so strong is the affinity of chlorine for hydrogen that it will extract it from many of its compounds. Thus, if turpentine, $C_{10}H_{16}$, be introduced into chlorine, the chlorine combines with the H and the C is set free in the form of soot, carbon not combining with chlorine under these conditions.

EXPERIMENT.—Into a cylinder of chlorine, introduce a strip of filter paper that has had a few drops of turpentine put on it. (The gas must be fairly pure for this experiment.)

Introduce a burning taper into another cylinder of the gas. Why does it burn? Why is the flame so smoky?

Chlorine, in presence of water, has a powerful bleaching and disinfecting action.

EXPERIMENT.—Place a piece of moist Turkey-red cotton, or a moistened colored flower in a cylinder of chlorine. If the experiment be repeated without moistening the cotton and flower, a difference in the action will be observed. What is it? How do you explain it?

Strips of colored cotton, or flowers, introduced dry into chlorine are not much affected, but if moist they are rapidly bleached. This is due to the fact that chlorine acts slowly on water, combining with the hydrogen and setting free the oxygen:

$$H_2O + 2Cl = 2HCl + O,$$

and it is this oxygen that does the bleaching, converting the colored compounds into colorless oxidised products. It may be asked, why should this oxygen do the bleaching when the oxygen in the air did not destroy the color of the cotton or flowers? It is known that in a great many cases elements *just set free from combination* exhibit an unusual degree of activity and therefore a name has been given to this condition: it is called the *nascent state,* from a Latin word meaning to be born. If we bring the atomic and molecular theories to bear on this peculiar phenomenon, they give us a mental picture of what may be the actual state of things, that is very useful. We know, from its molecular weight, that oxygen atoms usually occur in couples forming molecules, O_2. When, however, oxygen is just being liberated from combination in H_2O, for instance, it must appear as single atoms, at least for an instant. If, before these single atoms pair off, something is presented to them with which they can combine, they are much more likely to combine with it then than they would be after they themselves have combined into pairs; because, in this latter case, the combination of the oxygen with the other substance must be preceded by the decomposition of the already-existing oxygen molecules. The disinfecting action of chlorine is to be explained in a similar way, the germs being really destroyed by oxygen liberated from water present.

Even at ordinary temperatures, chlorine combines rapidly with many substances—many of the metals, especially when in a state of fine division, take fire spontaneously in chlorine, their chlorides being produced. (Compare metals in oxygen —oxides.)

EXPERIMENT.—Into one of the cylinders of chlorine prepared in the preceding experiment, shake a little powdered antimony. What happens? What is formed?

Commercial Methods of Preparing Chlorine.—As large quantities of chlorine are used in the industries for bleaching purposes (and for disinfecting), several methods have been developed for producing it on the large scale as cheaply as possible. In one of these, *Weldon's process,* a solution of hydrochloric acid is run into sandstone boxes, called chlorine stills, containing manganese dioxide; steam is admitted to heat the mixture and the reaction takes place according to an equation already given. Manganese dioxide, however, is an expensive substance, so, after the reaction is at an end, the residue, consisting mainly of a solution of $MnCl_2$, is run off into a special tank where it is treated with lime, and then steam and air are blown through it. This converts the $MnCl_2$ into a compound technically known as Weldon mud and very similar to MnO_2 in its behaviour with HCl. It is run back into the stills and used over again. (All the Cl that was in combination in the $MnCl_2$ is lost, so that, even under theoretically perfect conditions, this method yields only half the Cl originally present in the HCl.)

In *Deacon's process*, gaseous HCl and air are passed through large cast-iron cylinders filled with bits of brick that have been saturated with a solution of copper chloride and dried. The cylinders are heated from outside and about 80% of the HCl is decomposed according to the equation :

$$2HCl + O = H_2O + 2Cl$$

If there were no bricks and copper chloride in the cylinders, this same reaction would take place, but extremely slowly—so slowly that the process would be of no practical value at all. Just how the copper chloride hurries it up is not understood, but that it really does is very well known. The copper chloride acts here as a catalytic agent (see p. 28). Of late years a number of *electrolytic methods* for the production of chlorine have been introduced. In some of these a direct current is passed through a solution of salt in water, in others through fused salt. Chlorine is one of the products.

Chlorine for industrial purposes is sometimes supplied in the liquid form in strong steel cylinders. It is usually, however, driven into slaked lime, forming with it a compound, "chloride of lime," or bleaching powder, which is easily handled and from which the chlorine (or part of it) is easily liberated when wanted.

HYDROCHLORIC ACID

Historical.—The preparation of this compound was described by the German chemist Glauber, in 1648; but it is probable that it was known before his time. He called it "spirit of salt." Priestley studied it in 1772 and, because he produced it from sea-salt, called it "marine acid air"; to this day it is often called muriatic acid (Latin, *muria*, brine).

Occurrence.—It occurs in small proportions in the exhalations of some volcanoes and in very minute quantities in the gastric juice.

Preparation.—It may be prepared from its elements, as indicated above, but in practice it is always made by treating sodium chloride with sulphuric acid.

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

On the commercial scale this is carried out in great furnaces (as part of the Leblanc soda process, see p. 197), but in the laboratory it may be effected as follows:

EXPERIMENT.—Fit up an apparatus similar to that used in the preparation of chlorine (Fig. 13, p. 87). Place in the flask about 15 gr. of dry salt and cover this with strong sulphuric acid. Warm gently and collect the gas by downward displacement in dry cylinders. Why is this method of collecting used, and why is it possible? Test the gas in one cylinder with a burning taper. Does it burn? Does it support combustion? Invert another cylinder of the gas so that its mouth is under the surface of some water in a dish. What happens? Why? Does the cylinder fill with water completely? Why? Put some water into a cylinder and place the delivery tube from which the hydrochloric acid is issuing just above the surface of the water. Why not below? After some time, test a little of the water with blue litmus. What happens? What does it mean? To some more add a few drops of solution of silver nitrate. What happens?

The method of preparing hydrochloric acid just described is an example of a rather general method of preparing acids, *i.e.*, by treating a salt of the acid (*i.e.*, the acid in which hydrogen has been replaced by a metal—see p. 106) with some other acid which, under the conditions of the experiment, behaves as though it were stronger than the acid in combination and robs it of its metal, driving the weaker acid out. The reaction is an ordinary metathetical one. (See p. 105.)

Properties.—Hydrochloric acid is a gas, colorless, with a suffocating odor and a strong sour taste, slightly heavier than air; the G.M.V. weighs 36.5 gr., hence 36.5 is the molecular weight of the compound. It is extremely soluble in water, 1 volume of the latter dissolving about 500 volumes of the gas under ordinary conditions. (It should be remembered that the *solubility of gases* increases with pressure, but decreases with rise in temperature.) It is this aqueous solution that is sold as hydrochloric or muriatic acid.

Hydrochloric acid is a very stable compound (as we should expect from the eagerness with which it is formed from its elements); it does not burn, nor does it support combustion. In aqueous solution, it is one of the strongest acids known, possessing all the properties characteristic of that class of compounds. (See p. 103.) Its salts are called chlorides, and the solutions of all chlorides, including hydrogen chloride itself (HCl) give a white precipitate with silver nitrate solution.

$$NaCl + AgNO_3 = NaNO_3 + AgCl$$

A metathetical reaction takes place whereby two new substances are produced; one of these, silver chloride, is insoluble in water, and therefore separates out in the solid state. The separation of an insoluble substance from a solution is called *precipitation*, and the substance itself is called a *precipitate*.

Composition of Hydrochloric Acid.—Just as the composition of water was determined in two general ways, *i.e.*, by analysis and by synthesis, so the composition of hydrochloric acid may be determined by breaking it down or by building it up.

When an aqueous solution of HCl is electrolysed in an apparatus similar to that pictured in Fig. 6, p. 38, hydrogen is given off at one pole and chlorine at the other. At first the chlorine dissolves in the water, but after the water is saturated, and if very special precautions be taken, which need not be described here, it is found that hydrogen and chlorine are evolved in equal volumes. On the other hand, if equal volumes of hydrogen and chlorine are brought together and allowed to combine, it is found that none of either is left over—and the volume of the hydrochloric acid gas formed is exactly equal to the sum of the volumes of the two original gases. Hence, we may write

$$\text{1 vol. H} + \text{1 vol. Cl} = \text{2 vols. HCl (experiment)}$$
$$\text{1 mol. H} + \text{1 mol. Cl} = \text{2 mols. HCl (Avogadro)}$$

and from this we see that the molecule of hydrogen and the molecule of chlorine must each contain 2 atoms, as has already been pointed out in the case of oxygen (p. 74). So we may write

$$H_2 + Cl_2 = 2HCl,$$

because we know, from a careful study of the reaction, that this represents facts (expressed, of course, in terms of the molecular and atomic theories). Hydrochloric acid, then, is composed of hydrogen and chlorine in the proportion of one atom of the one to one atom of the other.

It is quite permissible to write

$$H + Cl = HCl,$$

because there is very little doubt—on account of the fact that hydrogen and chlorine do not combine in the dark, for instance—that the molecules of the hydrogen and chlorine must be decomposed—by light, or heat, or otherwise—before the atoms can combine as hydrochloric acid. It is probable, therefore, that the whole truth is something like this:

$$H_2 + Cl_2 = 2H + 2Cl = 2HCl$$

Hence, the equation given a few lines above,

$$H_2 + Cl_2 = 2HCl,$$

really represents the beginning of the reaction and the end, with the middle left out.

Similar considerations explain why it is necessary to apply heat to a mixture of oxygen and hydrogen before the two elements will combine. They are already combined—each with itself—and it is necessary to destroy this combination (in a portion of the mixture) by heat before the new combination can begin to take place.

Valence.—If we consider the formulas for two compounds that we have already studied, and two that we shall come across later on :

Hydrochloric acid	ClH	Ammonia	NH_3
Water	O	Methane	CH_4

we see that they record that it has been found that one atom of Cl, O, N, and C holds in combination 1, 2, 3, 4 atoms, respectively, of H. Apparently, then, an atom of carbon has the power of holding on to a great deal more hydrogen than an atom of chlorine has. Examples of this kind of thing are met with very frequently ; and so, for convenience, we give it a name :

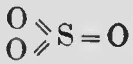
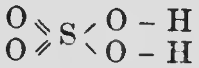
Valence *is that property by virtue of which an atom, or a group of atoms, is capable of holding in combination a definite number of other atoms.*

Atoms of different elements vary in their valence (or quantivalence, quantity of valence, as it is sometimes called), and atoms of the same element, under different conditions, sometimes exhibit different valences. However, there is generally one particular valence that is more or less characteristic of a certain element. Here, as elsewhere, if we wish to express ourselves quantitatively, we must select a standard and express other quantities in terms of this standard. The atom of hydrogen has been chosen for this purpose, and its valence is called one. Any atom that combines with (or replaces) one atom of hydrogen is said to be monovalent, or univalent, and is called a monad. The following table gives the terms used in this connection :

No. of H Atoms held or replaced	Adjectives	Nouns
1	Monovalent	Monad
2	Divalent	Diad
3	Trivalent	Triad
4	Tetravalent	Tetrad
5	Pentavalent	Pentad
6	Hexavalent	Hexad
&c.	&c.	&c.

Unfortunately different authors have used different terms in some cases; thus, univalent is often used for monovalent, bivalent for divalent, etc., but these are easily understood.

To determine the valence of an atom (or group of atoms), we find out how many atoms of hydrogen it will hold in combination. If, however, it does not form a compound with hydrogen, we may find out how many atoms of some other monovalent element, such as chlorine, it will combine with. Thus, the chloride of zinc is found to be represented by the formula $ZnCl_2$; hence, zinc is a diad.

These relations are often represented graphically thus: H – Cl, H – O – H, the lines representing by their number the valence of the element whose symbol they touch. Thus, H and Cl are monovalent and O is divalent. The atom of sulphur combines with 3 atoms of O, each of which is a diad, to form SO_3; hence, its molecule may be represented  $\begin{matrix}O\\O\end{matrix}\!\gg S = O$ and the molecule of H_2SO_4, derived from it,  $\begin{matrix}O\\O\end{matrix}\!\gg S \begin{matrix}\diagup O - H\\ \diagdown O - H\end{matrix}$ These are called graphic formulas, but only a very careful study of compounds enables us to write them correctly.

Chlorine forms three oxides, Cl_2O, ClO_2 and Cl_2O_7; and four acids containing oxygen (all acids must contain hydrogen), *i.e.*, $HClO$, $HClO_2$, $HClO_3$, $HClO_4$. These acids are a very good example of the law of multiple proportions, quantities of oxygen bearing very simple relations to one another being in combination with a fixed quantity of HCl. $HClO_3$, chloric acid, has as one of its salts, $KClO_3$ potassium chlorate, from which we prepared oxygen.

Chemical Nomenclature.—Unfortunately for modern convenience, a great many chemical substances were discovered and named long before anything was known about their composition, and others were named when wrong views were held with regard to their composition—and many of these old names are still in use. This makes chemical nomenclature rather confusing for the beginner. Still, there are a few rules (with some exceptions) that are useful. Some of these may be well illustrated by the acids of chlorine and their salts:

FORMULA OF ACID	NAME OF ACID	NAME OF SALT
HCl	*Hydro*chlor*ic*	Chlor*ide*
$HClO$	*Hypo*chlor*ous*	*Hypo*chlor*ite*
$HClO_2$	Chlor*ous*	Chlor*ite*
$HClO_3$	Chlor*ic*	Chlor*ate*
$HClO_4$	*Per*chlor*ic*	*Per*chlor*ate*

When an acid contains no oxygen, its name begins with hydro - and ends with - ic.

The termination - ous, in the name of an acid, indicates less oxygen than the termination - ic. The prefix hypo - (used with the termination - ous) indicates still less oxygen than - ous; and the prefix per - (used with the termination - ic) indicates more oxygen than - ic.

In naming salts of acids, the salt of an acid containing no oxygen has a name ending in - ide, the hydro - of the name of the acid being dropped. The termination - ide, therefore, indicates absence of oxygen (except in the word oxide). In naming the salts of oxygen acids, the - ous of the name of the acid is changed into - ite, and the - ic into - ate. If the acids have the prefix hypo - or per -, this is retained in the name of the salts.

Classification of the Elements.—A great many elements are known—they are given in the list on the inside of the back cover, and there are several other doubtful ones—*i.e.*, substances that chemists have not yet succeeded in decomposing, but which may turn out to be compounds when further worked with. If all these elements were as different as oxygen, hydrogen and chlorine are, their study would be very complicated. Fortunately, however, this is not the case, as we often find elements that resemble one another very strongly. Various classifications have been tried, none of them perfect, so as to bring out as clearly as possible the relations of the elements, and one of these we shall consider now.

First, the elements are divided into two large classes—the metals and the non-metals; the metals. combining with oxygen and hydrogen to form bases (see p. 104), are called base-forming elements, and the non-metals, combining with oxygen and hydrogen to form acids, are called acid-forming elements. Further, it is found that the elements under these two headings can be grouped into a number of families, the members of each of which bear certain striking resemblances to each other.

The acid-forming elements, or non-metals may be grouped as follows :

Chlorine Family	Sulphur Family	Nitrogen Family	Carbon Family
Fluorine Chlorine Bromine Iodine	Sulphur Selenium Tellurium	Nitrogen Phosphorus Arsenic Antimony	Carbon Silicon Titanium

These groups do not include quite all the non-metals. Hydrogen seems to be an element by itself—it has no near relations. Boron is more or less alone, though it somewhat

NOTE

resembles silicon and titanium—a sort of cousin, not a brother. And then there are five extraordinary elements, helium, neon, argon, krypton and xenon, all gases, that are certainly not metals, but they are not acid-forming, as they never form any compounds at all—even their molecules consist of single atoms, so averse are these particles to any sort of combination.

A classification of all the elements much more thorough-going than the one indicated above is what is termed the Periodic Arrangement. Although not entirely satisfactory, it is by far the best classification that has been developed up to the present time. It is, however, too complicated for our present purpose and therefore larger books must be consulted by those who care to study it.

The Chlorine Family.—As we have just seen, there are four elements, fluorine, chlorine, bromine, iodine, which are said to form a natural family of elements: that is, they exhibit very strong resemblances to each other, mainly in their chemical behaviour, although in their physical properties also there are well-marked gradations. They are called halogens (salt producers). None of them occur free in nature.

ELEMENT	AT. WT.	VALENCE	STATE	COLOR	ACTIVITY	COMP'D WITH H
Fluorine .	19	1	gas	Pale yellow	enormous	HF
Chlorine .	35.5	1	gas	Yellowish-green	great	HCl
Bromine .	80	1	liquid	Red brown	not great	HBr
Iodine . .	127	1	solid	Gray-black	slight	HI

The only other non-metal that has a valence of 1 is hydrogen.

Bromine.—This element was discovered in 1826 by a Frenchman named Ballard, who obtained it from "bittern," the liquid left after common salt has crystallised out from concentrated sea-water. This bittern contains bromides, and bromine is obtained from them, as chlorine is obtained from chlorides:

$$2KBr + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + 2Br$$

EXPERIMENT.—Place a little manganese dioxide in the bottom of a test-tube and with it a crystal of potassium bromide about half the size of a pea. Add a few drops of sulphuric acid and warm gently. Be careful not to breathe much of the fumes.

If this reaction is carried out in a retort with the neck inserted in a flask kept cold by water pouring over it, liquid bromine is obtained. Bromine may also be obtained by treating a bromide with chlorine, the latter driving out the bromine—a good example of replacement.

$$KBr + Cl = KCl + Br$$

Bromine under ordinary conditions is a heavy liquid (with the exception of mercury, the only element liquid at ordinary temperatures), of a dark reddish-brown color and having a very pungent odor, whence its name, from the Greek *bromos*, a stench. It evaporates very easily, giving a vapor of lighter shade than the liquid. It is less active than chlorine, but combines slowly with hydrogen to form HBr, hydrobromic acid, a gas very similar in properties to HCl. The salts of this acid are called bromides, the most important being potassium bromide, KBr, used in photography and in medicine.

Iodine.—This also was discovered by a Frenchman, Courtois, in 1812. He prepared it from "kelp," the ashes of sea plants. It occurs to a very small extent in sea-water, whence the sea plants extract it. It is also found in small quantities in Chili saltpetre (see p. 132), which is supposed to have been derived from the decay of sea plants. It may be prepared from iodides as bromine and chlorine are prepared from bromides and chlorides.

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + 2I$$

EXPERIMENT.—Proceed as in the preceding experiment, substituting potassium iodide for the bromide, and keeping the upper part of the test-tube from becoming heated. What vapors are formed? What forms on the upper part of the tube? How did it get there?

It is a gray-black, shiny solid which on heating gives a beautiful purple vapor (Greek, *ioeides*, violet-like). It is slightly soluble in water, like chlorine and bromine, and very soluble in alcohol, this solution being known as tincture of iodine (it contains also a small quantity of potassium iodide). Free iodine gives a blue color with solution of starch. Iodine is less active than bromine and combines only extremely slowly with hydrogen, and the compound is quite unstable; it is a gas, HI, hydriodic acid, and its physical and chemical properties are very similar to those of hydrochloric and hydrobromic acids. Its salts are called iodides, the most important being potassium iodide, KI, used in photography and in medicine.

Fluorine.—Although compounds of fluorine have been known for a very long time, all attempts to isolate the element failed. Finally, Moissan, the great French chemist who died only recently, succeeded in preparing free fluorine in 1891.

Fluorine occurs in nature principally as fluor-spar (Derbyshire spar, blue John), CaF_2. This substance is called fluorspar (Latin, *fluo*, I flow) because it was used in metallurgical operations to make slags flow well. Fluorine is also found in combination in some other minerals, in bones (particularly in the enamel of the teeth), and in minute traces in the blood and in milk.

It is prepared from hydrofluoric acid by an electrical method in platinum apparatus, everything being kept at a very low temperature (about – 25°) so as to prevent the fluorine from attacking the apparatus.

It is a gas, pale yellow in color, and is the most active substance known, attacking almost everything at ordinary temperatures.

Even solid fluorine at a temperature of – 252°, if brought into contact with liquid hydrogen at the same temperature, produces a most violent explosion and the highly resistant platinum, of which the apparatus is made in which fluorine is prepared, is slowly attacked by it at – 25°. At ordinary temperatures it attacks silicon, boron, lamp-black, etc., and almost all the metals, but under no conditions will it combine with oxygen. It is a most dangerous substance to work with.

Hydrofluoric Acid (HF) is prepared by acting on powdered fluor-spar with sulphuric acid in a lead or platinum dish. If a watch-glass be covered on the convex side with a layer of paraffin or beeswax, some device or letters be scratched through this with a pointed piece of wood, and the watch-glass be laid, waxed side down, on the dish and left there for some hours, on removing the wax the device or letters will be found etched into the glass. Hydrofluoric acid is a colorless liquid that boils at 19° (about the temperature of an ordinary room); its vapor is extremely poisonous, and when the acid or its solution is brought into contact with the flesh it produces blisters and sores that are very hard to heal. It is soluble in all proportions in water, and the commercial article is about half water and half HF. The most interesting and useful property of the acid is its power of attacking glass, combining with the silicon in the glass to form gaseous silicon tetrafluoride, SiF_4, which passes off, leaving the glass etched. On account of this property, the acid cannot be kept in glass bottles, but is kept in bottles made of platinum, gutta percha, or ceresine, a sort of hard mineral wax. The divisions on fine thermometers, burettes, and other glass measuring instruments, are made by a method similar to that employed in the experiment given above.

QUESTIONS

1. Do you know of any cases of combustion in which oxygen is not involved? Describe such a case, showing how it fulfils all the requirements of the definition of the term combustion.
2. Why would it not be a good method to prepare HCl from Cl?
3. Write the equation representing what would take place if sulphuric acid were allowed to act on potassium chloride.
4. Compare the elements fluorine, chlorine, bromine, iodine, as to (*a*) occurrence, (*b*) preparation, (*c*) properties, (*d*) compounds.

5. Why do you think the elements fluorine, chlorine, bromine, iodine, are classed together as forming a family of elements?

6. Could hydrochloric acid be collected in the ordinary way over the pneumatic trough? Why?

7. Mention a direct and an indirect way of preparing chlorine from common salt.

8. List the properties of chlorine.

9. What is the valence of each element in the following compounds: H_2S, H_3P, HBr, P_2O_5; and of the groups enclosed in brackets in: $H(NO_3)$, $H_3(PO_4)$, $H_2(SO_4)$, $H_4(P_2O_7)$?

10. How could you distinguish a chloride, a bromide and an iodide from each other?

11. What is an oxidising agent? Why is MnO_2 called an oxidising agent? Show how it acts as one in the production of chlorine.

12. What facts would lead us to think that elements just liberated from combination are chemically more active than at other times? How do you explain this? What name is given to an element in this condition?

13. In preparing chlorine from HCl what oxidising agent is used in Weldon's process? In Deacon's process? Which oxidising agent is the cheaper? Which method is the more efficient? Can you think of any reason why, possibly, the Weldon process can compete with the Deacon?

14. The word gas is derived from the same root as the word ghost. Can you think of any reason why hydrochloric acid was called spirit of salt?

15. Can you imagine a reason why hydrogen and chlorine will combine in the light but not in the dark?

16. How much MnO_2 is required to produce 1000 gr. of chlorine from HCl? What would be the volume of the gas at S.T.P.?

17. Ordinary hydrochloric acid solution contains 40% HCl. How much would be required to produce 100 gr. ferrous chloride and what volume of hydrogen at 740 mm. and 18° would be produced at the same time?

$$Fe + 2HCl = FeCl_2 + 2H$$

18. What volume of air ($\frac{1}{5}$ oxygen) would be required to produce 1000 litres of chlorine by the Deacon process?

CHAPTER X

ACIDS. BASES. SALTS. NEUTRALISATION. ELECTROLYTIC DISSOCIATION

We have already had a few instances of the value of classification—we are to have another. The number of chemical compounds known is very large, probably between 150,000 and 200,000. Hence, it is highly important that we should be able to classify them in some way, if we ever expect to be able to remember much about them. Various classifications have been tried; some have proved quite valueless, others suitable for one purpose, still others for another.

There are three large classes of compounds which it will be well for us to become acquainted with at once—we have had to mention them already—*i.e.*, acids, bases and salts. Of course, these three classes do not include anything like all compounds, but, with anhydrides which we shall meet with later on, they embrace most of the compounds we shall study here.

In the work that we have done so far, we have studied hydrochloric acid, a gas, and have used sulphuric acid, a liquid. Many of us know also citric and tartaric acids, two white solids sometimes used in making cheap "lemonade." Acids then may be solids, liquids, or gases—what is it that brings them all into one class? There are four points which, taken together, distinguish them from other compounds:

An Acid (1) *is a compound containing hydrogen.*
(2) *Its hydrogen is easily replaced by a metal.*
(3) *Its solution has a sour taste.*
(4) *Its solution turns blue litmus red.*

Taking hydrochloric acid, HCl, as an example, we already know (1) that it contains hydrogen. From its reaction with zinc (p. 39), we have seen (2) that its hydrogen may be replaced by a metal. If we add a drop or two to a test-tube full of water, stir well, and carefully place a drop on the tongue, we shall find (3) that its solution has a sour taste. And, by putting a drop or two of blue litmus solution into this dilute acid solution, we shall notice (4) that the litmus is turned red. This last is known as an *acid reaction.*

Now, the members of a second class of compounds, called bases, are in a certain sense the opposite of acids:

A Base (1) *is a compound containing hydroxyl, OH.*
(2) *Its hydroxyl easily combines with the H of an acid to form water.*
(3) *Its solution has a soapy taste.*
(4) *Its solution turns red litmus blue.*

Caustic soda, NaOH, is a typical base; and we must for the present take on trust the statements that (1) it contains hydroxyl, and (2) this hydroxyl easily combines with the hydrogen of an acid. But, if we dissolve a little piece about the size of the head of a large pin in half a test-tube full of water, we can then observe that (3) its solution has a soapy taste; and, by just reddening some litmus solution with the least possible quantity of acid, and then dropping some of this into the test-tube, we shall see that (4) the solution turns the red litmus blue. This last is known as a *basic* or *alkaline reaction.*

(*Note.—All tasting experiments must be made with very great caution.*)

Experiment.—Dissolve about 40 gr. of NaOH in a litre of water; add about 100 cc. of strong hydrochloric acid to another litre of water. Set up two burettes in stands and fill one with the soda solution and the other with the hydrochloric acid solution, bringing both to zero by letting the excess run out into a beaker. Now run 20 cc. of the acid solution into a clean flask and add just enough litmus solution to give it a distinct color. Into a second flask put 20 cc. of the basic solution and add litmus as before. Fill each burette to the zero mark with its proper solution and then slowly add acid from the burette to the base in the flask, swirling constantly, until the litmus is neither blue nor red—called neutral. To the acid in the other flask, add base from the other burette until neutralised. Note the volumes of solutions used. Repeat the experiment, this time beginning by running out 30 cc. of acid and base respectively into the flasks. Again note results and see how they agree with the former. It takes a little practice to get the color changes just right, but the results obtained will be near enough to illustrate the general principle involved, *i.e.*, that a definite quantity of acid neutralises a definite quantity of base. Evaporate some of the neutral solution to dryness and notice the salt obtained. The reaction involved in the experiments just performed is represented, qualitatively and quantitatively, by the equation :

$$HCl + NaOH = HOH + NaCl$$

The reaction between HCl and NaOH is an example of a sort of chemical change called a metathetical reaction, metathesis, or double decomposition.

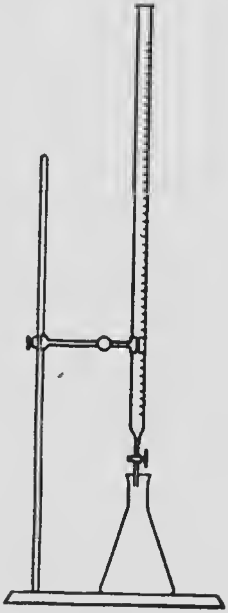


FIG. 14.

Metathesis *is the reaction that takes place when two compounds react with one another in such a way that part of one combines with part of the other, and the rest of the one with the rest of the other.* (It may be graphically described as "change partners.")

Analysis, synthesis, substitution and metathesis, form the four principal classes of chemical actions.

An acid owes its acid properties to the H which it contains, and a base its basic properties to the OH. (Hydroxyl is not known in the free state any more than atomic hydrogen is.)

Neutralisation.—*When an acid is added to a base, both in solution, the main thing that happens is that the acid hydrogen combines with the basic hydroxyl to form water, which is neither acid nor basic, but neutral.* The rest of the acid may then combine with the rest of the base to form what is known as a salt, which may be defined in several ways, one of which is:

A Salt *may be regarded as an acid in which the acid hydrogen has been replaced by a metal* (or metallic radical, see p. 203). There are acid and normal salts; these will be defined later (p. 122). The salt is spoken of as a salt of the acid from which it has been (theoretically) formed; it is also said to be a salt of the metal, or base. Thus, sodium chloride, NaCl, is said to be a salt of hydrochloric acid and of sodium.

The theory of electrolytic dissociation tells us that when an acid is dissolved in water its molecule is split up into the hydrogen atom (or atoms, each) with a positive charge of electricity, and the rest of the molecule, with a negative charge (or as many negative charges as there have been hydrogen ions formed). These charged particles are called ions and the production of them ionisation. The positively charged ions are called *kations* and the negatively charged ones *anions*. When a base is dissolved its molecule is similarly ionised, the hydroxyls taking the negative charges and becoming anions, and the rest of the molecule, generally the atom of a metal, taking a corresponding positive charge, or charges, and forming the kation.

$$HCl = H^{+} + Cl^{-}$$

$$H_2SO_4 = H^{+} + H^{+} + SO_4^{=}$$

$$NaOH = Na^{+} + OH^{-}$$

$$Ca(OH)_2 = Ca^{\overset{+}{+}} + OH^{-} + OH^{-}$$

When the solution of the acid comes into contact with the solution of the base, the H^{+} ions combine with the OH^{-} ions to form HOH, the positive electricity of the H ions neutralising the negative electricity of the OH ions, leaving the HOH uncharged. The anions of the acid and the kations of the base generally remain unchanged in the solution.

$$H^{+} + Cl^{-} + Na^{+} + OH^{-} = HOH + Cl^{-} + Na^{+}$$

If the water be evaporated off, however, they combine to form a salt and their charges neutralise one another and disappear. Conversely, when a salt is dissolved in water, its molecules are split up into positively charged ions, kations (metal) and negatively charged ions, anions (acid radical).

$$NaCl = Na^{+} + Cl^{-}$$

$$CuSO_4 = Cu^{\overset{+}{+}} + SO_4^{=}$$

According to this theory, we may define the terms acid, base and salt in a very simple manner :

An Acid *is a compound that gives H ions on solution in water.*

A Base *is a compound that gives hydroxyl ions on solution in water.*

A Salt *is a compound that gives positive and negative ions other than H and OH on solution in water.*

There are a great many compounds which are not ionised at all on solution in water, such as sugar, alcohol, glycerine. They are not acids, bases, or salts.

Solutions of acids, bases and salts (*i.e.*, solutions which conduct electricity) are called *electrolytes*, and the way in which they conduct the current may be explained in terms of the theory of electrolytic dissociation as follows: Suppose an apparatus like that pictured in fig. 6, p. 38, be set up, the terminals of the wires are called *electrodes*, that of the positive wire, the *anode* and that of the negative wire, the *kathode* (Greek, *kata*, away from, *hodos*, a way); then, if the electrolyte be a solution of HCl, the positively charged H ions are attracted to the negatively charged kathode, and the negatively charged Cl ions to the positively charged anode. At the electrodes, the ions give up their charges, using up (neutralising) in so doing an equivalent quantity of negative and positive current which runs in from the battery; the uncharged atoms then form molecules and appear as ordinary hydrogen and chlorine on the kathode and anode respectively. The original hydrochloric acid has thus been decomposed into hydrogen and chlorine. Such decomposition, brought about in an electrolyte by an electric current, is known as *electrolysis.*

It must be very carefully borne in mind that the electric current has nothing to do with the **Production** *of the ions this is somehow caused by the solvent (water) alone--the current merely makes use of the ions which it finds ready made.*

In many cases of electrolysis, secondary reactions occur. Thus, if a solution of H_2SO_4 be electrolysed (as was done in the experiment on p. 38), hydrogen is liberated at the kathode and SO_4 at the anode; but the uncharged SO_4 cannot exist alone and immediately reacts with water, thus :

$$SO_4 + H_2O = H_2SO_4 + O,$$

free oxygen appearing at the anode. Or, if a solution of NaOH be electrolysed, we should have at the anode the secondary reaction

$$OH + OH = H_2O + O,$$

and at the kathode,

$$Na + H_2O + = NaOH + H$$

The final products would therefore be oxygen and hydrogen (really derived from the water), the original quantity of NaOH being constantly reformed and re-ionised (just as was the case with the H_2SO_4 in the previous experiment).

Pure water is almost un-ionised (only extremely small quantities of OH and H ions are present in it); hence, pure water is practically a non-conductor.

Many salts, when fused, will conduct a current and may therefore be electrolysed. It is supposed that the main part of the fused mass acts as water does, *i.e.*, as a solvent, and that the small remainder of the salt is electrolytically dissociated by it, existing as ions which conduct the current, as described above. Thus, if a current be passed through fused NaCl, common salt, sodium is obtained at the kathode and chlorine at the anode. This process is used on the commercial scale.

Metals are often deposited from solutions of their salts by means of the electric current, and this sort of electrolysis is called electroplating. Thus, if a brass object, such as a pencil-holder, be made the kathode in a solution containing a salt of nickel, the nickel kations will be attracted to this pencil-holder kathode, there discharged, and a coating of nickel deposited: the object is nickel-plated. In certain cases, metals are obtained from their ores by dissolving them in suitable solvents and then depositing them in the metallic state electrolytically.

There is, as yet, no satisfactory theory as to why the water ionises acids, bases and salts on solution.

The theory of electrolytic dissociation was enunciated by the great Swedish chemist, Arrhenius, in 1887, to account for a large number of phenomena, both chemical and electrical. It did this so satisfactorily that it brought about almost as great a change in chemistry as the enunciation of the atomic theory of Dalton did.

QUESTIONS

1. A solution of sodium hydroxide is prepared having 40 gr. of the hydroxide in 1 litre of the solution, and a certain volume of this is found to exactly neutralise an equal volume of a solution of hydrochloric acid. How much HCl is there in 1 litre of the latter solution?

2. 18 cc. of the solution of NaOH mentioned in the preceding question neutralises 23 cc. of a solution of nitric acid. What is the strength of the latter solution (*i.e.*, how many gr. of HNO_3 are there per litre)?

3. A solution of potassium hydroxide (KOH) is exactly neutralised with sulphuric acid. The solution is then evaporated to dryness and the residue is found to weigh 96 gr. How much potassium hydroxide and how much sulphuric acid were used?

4. Write equations representing the neutralisation of each of the following bases by each of the acids:

KOH	HCl
$Ca(OH)_2$	H_2SO_4
$Fe(OH)_3$	H_3PO_4

5. To explain what sort of facts do you think the theory of electrolytic dissociation was formulated?

6. Some potassium hydroxide, KOH, is dissolved in water, and some nitric acid, HNO_3, in another portion of water; the two solutions are then mixed in proper proportions to neutralise each other. Explain, in terms of the electrolytic dissociation theory, what happens (*a*) when the KOH is dissolved, (*b*) when the HNO_3 is dissolved, (*c*) when the two solutions neutralise each other.

7. Describe how a clean iron article might be electroplated with copper, explaining what takes place.

CHAPTER XI

SULPHUR AND ITS COMPOUNDS

History.—As sulphur occurs free in a good many parts of the earth, and in considerable quantities, it has been known from very early times ; and, on account of its inflammability, it has always aroused a good deal of curiosity and interest. The alchemists believed that it was a constituent of all metals (which of course it is not) and was the cause of their alterability in the fire. On account of the fact that sulphurous fumes are given out from volcanoes and cracks in the rocks in volcanic regions, vast deposits of ever-burning sulphur were supposed to exist deep down in the earth, and have played a considerable part in the superstitions of many races.

Occurrence.—The term native, as used in mineralogy, means free or uncombined, and native sulphur, as has already been said, is found in many parts of the world, particularly in Sicily and Louisiana. Sulphur also occurs in combination with many metals, forming sulphides, and some of these sulphides are among the most valuable ores. Iron pyrites, or pyrite, FeS_2, sometimes called "fool's gold" on account of its yellow color, is one such sulphide ; it is not much used as an ore of iron, however, but as a source of sulphur compounds as we shall see later. Chalcopyrite, or copper pyrites, $CuFeS_2$, is one of the most important ores of copper, and galena, PbS, of lead. There are also a number of sulphates which occur in large quantities in nature, perhaps the most important being gypsum, alabaster, $CaSO_4 . 2H_2O$. Sulphur occurs also in small proportions in the proteïds (protoplasm, albumen, etc., see p. 182) which form the basis of all living matter, both vegetable and animal, and also in such substances as oil of mustard, oil of garlic, bile, hair and wool.

Preparation.—Most of the sulphur of commerce comes from Sicily. Here the ore, which consists of sulphur mixed with useless rock, is piled up in large kilns and set on fire; by admitting a limited supply of air, part of the sulphur only is burned, but this produces sufficient heat to melt the rest, which trickles out of the mass and is collected at the lowest point of the kiln and run out. This crude sulphur is then refined by heating it in a large iron retort and passing the vapors into a brick chamber. At first, when the chamber is cool, the sulphur condenses on the sides in the form of little yellow rosettes, called "flowers of sulphur;" when these are scraped off, they fall to a fine yellow powder which is still called flowers (not flour) of sulphur. As the chamber gets hotter, the sulphur collects as a liquid on the floor, whence it is run off and cast in cylindrical wooden moulds, forming roll sulphur, or brimstone (German *brenn-stein*, burning stone).

Properties.—Sulphur is an allotropic element, being known in the solid state in three forms: rhombic sulphur, monoclinic sulphur, and plastic, or amorphous (non-crystalline) sulphur. These forms differ mainly in their physical properties and are described below.

Crystallography.—Most chemical substances, when in the solid state, possess a regular internal structure which is exhibited externally in regular polyhedral forms (in so far as their formation has not been interfered with by mutual pressure or the presence of other solid bodies) called crystals. These forms are very frequently used in identifying substances, particularly minerals. For purposes of study and description, these crystals are regarded as built up symmetrically round certain imaginary intersecting lines called axes; and they can be divided into six systems in accordance with the relative lengths and positions of these axes.

Regular or isometric system.—Three axes, all at right angles, all equal in length. (Forms, cube and regular octahedron.)

Tetragonal system.—Three axes, all at right angles, two equal, third longer or shorter. (Forms, square prism and pyramid.)

Orthorhombic system.—Three axes, all at right angles, no two equal. (Forms, rectangular prism and pyramid.)

Hexagonal system.—Four axes, three in one plane, all equal, and intersecting at angles of 60°, fourth axis perpendicular to the plane of the other three and of any length. (Forms, hexagonal prism and pyramid.)

Monoclinic system.—Three axes, two intersecting at an acute angle, third perpendicular to both these, all unequal. (Forms, inclined prism and pyramid.)

Triclinic system.—Three axes, no right angles, all unequal. (Forms, doubly inclined prism and pyramid.)

Solids that are not crystalline are called *amorphous* (Greek, *a*, without, *morphe*, form), and are really supercooled liquids rather than true solids.

Rhombic Sulphur.—Native sulphur, and roll sulphur prepared from it as described above, are made up of aggregates of rhombic crystals. This form of sulphur is a lemon-yellow solid; specific gravity, 2.06 (water = 1); melting point 114.5°. It is almost insoluble in water, but easily soluble in a liquid called carbon disulphide, CS_2. If such a solution be prepared and allowed to evaporate slowly, well-formed rhombic crystals of sulphur are obtained. In roll sulphur the structure is rhombic, but the crystals have crowded together in their growth (from the molten sulphur) so as to hide their external forms.

Monoclinic Sulphur.—If some sulphur be melted in a crucible (which will hold at least 100 cc.) and allowed to cool slowly, and if, as soon as a crust forms on the top, this crust be punctured and the still molten sulphur below be poured off, the crucible will be found to be lined with long transparent needles which are crystals belonging to the monoclinic system. This form of sulphur, which is honey-yellow, has a specific gravity of 1.96 and melts at 119°. Insoluble in water, soluble in CS_2. The crystals on standing at room temperature slowly become lemon-yellow and are then found to consist of an aggregate of minute rhombic crystals.

Rhombic and monoclinic sulphur can exist together unchanged for any length of time at a temperature of 95.4°. Below this temperature, the monoclinic form slowly turns into the rhombic, as has been described above, while above this temperature the rhombic form slowly changes into the monoclinic. Hence, this is called the transition temperature of rhombic and monoclinic sulphur.

Plastic or Amorphous Sulphur.—If either crystalline form of sulphur be melted, a thin pale-yellow liquid is obtained; if this be heated it becomes dark brown and so thick that it will hardly pour out of the vessel when inverted; heated still higher, it becomes less viscous, and boils at 445°. If this hotter liquid be poured into cold water, a gummy mass is formed, amorphous sulphur, which slowly hardens, changing into rhombic sulphur.

When any form of sulphur is heated sufficiently, it will burn in air or oxygen with a purple flame, forming the dioxide SO_2 (with traces of the trioxide, SO_3). Under certain conditions, sulphur will combine slowly with hydrogen. Even when cold, if rubbed together with many metals in a finely divided state, it will slowly combine with them, forming sulphides; when heated, it combines rapidly and vigorously with most metals (*e.g.*, iron, copper). In these ways, sulphur resembles oxygen in properties.

Sulphur is used in making gunpowder, fireworks, matches, and for preparing its compounds SO_2, H_2SO_4, CS_2, etc.

Hydrosulphuric Acid, H_2S, sulphuretted hydrogen. This occurs in the gases issuing from some volcanoes and in solution in the water of what are known as "sulphur springs." It is also produced when organic matter containing sulphur decays, and it is to this compound that rotten eggs and decaying cabbage owe their odor, in part.

When hydrogen is passed through boiling sulphur or overheated sulphides, a small quantity of H_2S is formed. This is of interest, though not of any practical importance, on account of its likeness to the production of H_2O from hydrogen and oxygen, or hydrogen and oxides when heated, sulphur appearing in this and in other ways similar to oxygen which belongs to the same family of elements. In the laboratory, sulphuretted hydrogen is usually prepared by the action of sulphuric or hydrochloric acid on iron sulphide, FeS (made by heating a mixture of iron and sulphur; pyrite, FeS_2, is useless for the preparation of H_2S).

$$FeS + H_2SO_4 = H_2S + FeSO_4$$

EXPERIMENT.—Set up a generator similar to that used in making hydrogen; put into the flask some pieces of iron sulphide and just cover them with water; add dilute sulphuric acid and collect the gas evolved over water, using the same precautions against explosion as in the case of the preparation of hydrogen. Test a bottle of the gas with a lighted taper and notice the color of the flame, the smell of burning sulphur and the deposition of sulphur in the bottle. How do you explain these phenomena? Bring a piece of filter-paper, moistened with a solution of lead acetate near the mouth of the delivery tube and notice the change in color. How do you explain it? Fill a small bottle half full of water and pass the gas into it for five minutes, with the mouth of the delivery tube under the water; withdraw the delivery tube, place the finger over the mouth of the bottle and shake. Note that suction is exerted. What does this indicate? Test the solution with blue litmus. What happens? What does it mean? Place a little solution of each of the following compounds in a separate test-tube and add some of the solution of H_2S: copper sulphate, cadmium sulphate, tartar emetic (a compound of antimony), zinc sulphate with excess of ammonia. What happens in each case? How do you explain it? Of what use might such actions be?

Hydrosulphuric acid is a colorless gas with a powerful odor similar to that of rotten eggs, and a peculiar sweetish taste. When inhaled in large quantities it is poisonous. It is heavier than air, the G.M.V. weighing 34 grs. It is soluble in water, 1 volume of the latter slowly dissolving about 3 volumes of the gas under ordinary conditions. Sulphuretted hydrogen burns in air or oxygen, H_2O and SO_2 being formed, and some S usually escaping unburned, owing to deficiency of oxygen. In solution, H_2S is slowly acted on by the dissolved oxygen from the air, the H being converted into H_2O and the S separating out in a very fine state of division, making the water look milky. There is a fundamental difference between this behaviour and that between chlorine and water.

In the case of H_2S the water itself is not decomposed, only dissolved oxygen reacting; chlorine, of course, decomposes the water itself, combining with the hydrogen. Some metals decompose H_2S slowly in the cold, combining with the S and setting free the H; thus, silver is blackened owing to the production of Ag_2S; other metals react similarly when heated in the gas. (Compare reactions of metals with H_2O.) The solution of H_2S in water exhibits a feeble acid reaction with litmus and will consequently neutralise bases. The acid is much used as a reagent in chemical analysis, because it reacts metathetically with the salts of many metals whose sulphides are insoluble in water, precipitating these sulphides, *i.e.*, the sulphides separate out in the solid state from the solution, and, as these sulphides often have characteristic colors, many metals in solution can be recognised in this way.

Sulphur Dioxide, SO_2, sulphurous anhydride. This compound issues from some volcanoes in large quantities.

As has already been said, H_2S occurs in the same way. When the two gases come from the same volcano and meet, the following reaction takes place,

$$2H_2S + SO_2 = 2H_2O + 3S$$

This is the way in which a great deal of the native sulphur of the world has been produced.

Sulphur dioxide is formed when sulphur is burned in air or oxygen. (See exp. p. 31.) It may also be prepared by heating together some metal, such as copper, and strong sulphuric acid. The usual reaction between a metal and an acid is the replacement of the hydrogen by the metal; this probably takes place here:

$$Cu + H_2SO_4 = CuSO_4 + 2H$$

but the hydrogen reacts with the hot, concentrated sulphuric acid, thus:

$$2H + H_2SO_4 = 2H_2O + SO_2$$

(In preparing hydrogen from sulphuric acid and zinc, the acid was used cold and dilute to prevent this second reaction.)

Another method of preparation is by the roasting of sulphide ores. *Roasting*, in chemical and metallurgical sense, is the act of highly heating something in a current of air for purposes of oxidation. Most sulphide ores are thus roasted to get rid of part or all of the sulphur before the smelting for the metal is undertaken.

$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2$$
$$ZnS + 3O = ZnO + SO_2$$

Formerly, all the SO_2 produced in this way was allowed to escape into the air and was thus not only lost, but did a great deal of harm to vegetation in the neighborhood of the smelters. Now a great deal of it is converted into sulphuric acid, as we shall see later. This is one of a great many cases of the economical use of substances that were formerly looked upon as waste products.

Sulphur dioxide is a colorless gas with a pungent odor (the odor of burning sulphur matches) and disagreeable taste.

Its boiling point under atmospheric pressure is −8° and under a pressure of 3.25 atmospheres, 20°; on this account it is very easily liquefied, and is sold for disinfecting and other purposes in metal cylinders, many of the smaller ones being made of ordinary "tin"—tinned iron.

Sulphur dioxide does not burn, nor does it support combustion; under ordinary conditions it unites with extreme slowness with oxygen to form SO_3. It is a valuable bleaching agent, being used to bleach straw goods, paper and even certain foods, such as canned corn and dried apples. It is also a much-used disinfectant, rooms in which cases of infectious diseases have occurred, or which have become infested with bed-bugs or other vermin, being disinfected by burning sulphur in them or introducing SO_2 from a cylinder. SO_2 dissolves in water, uniting with it to form an unstable compound, H_2SO_3, sulphurous acid. A great many oxides behave in this way and there are others which combine with water to form bases; such oxides are called anhydrides.

An Anhydride *is an oxide which will combine with water to form an acid or to form a base; those forming acids are called acid anhydrides, those forming bases, basic anhydrides.*

The salts of sulphurous acids are called sulphites. When treated with a stronger acid, such as sulphuric or hydrochloric, sulphurous acid is liberated and most of it breaks down into water and sulphur dioxide:

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2SO_3$$
$$H_2SO_3 = H_2O + SO_2$$

This, then, is a very easy way of preparing SO_2 in the laboratory.

The combination of sulphur dioxide and water to form sulphurous acid is what is called a reversible reaction, because sulphurous acid will break down into sulphur dioxide and water:

$$SO_2 + H_2O = H_2SO_3$$
$$H_2SO_3 = H_2O + SO_2$$

Such a reaction is often written as follows in order to indicate that it will proceed in one direction or the other, according to circumstances:

$$SO_2 + H_2O \rightleftarrows H_2SO_3$$

Other reversible reactions that we have already met with are

$$3O_2 \rightleftarrows 2O_3$$
$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 8H$$
$$H_2O + 2Cl \rightleftarrows 2HCl + O$$

Suppose we consider the reaction $SO_2 + H_2O \rightleftarrows H_2SO_3$ as taking place in a confined space. If SO_2 and H_2O are brought together, the action must go from left to right at first, because, just in the beginning, there is no H_2SO_3 formed to make possible any reaction from right to left. As the first reaction proceeds, however, the possibility of the reverse reaction becomes greater and greater. At first there will be more action from left to right than in the opposite direction; but as the quantity of H_2SO_3 becomes greater, there will also be more action from right to left, especially as the quantities of SO_2 and H_2O have been reduced. Finally, the rate at which H_2SO_3 molecules are splitting up will become equal to the rate at which they are being formed we have then a condition of chemical equilibrium. Suppose now that the vessel in which the reaction is taking place be opened—some of the gaseous SO_2 will escape and immediately there will be a hurrying up of the reaction from right to left to produce more SO_2 in order to re-establish the equilibrium which has been disturbed; if the escape of SO_2 be allowed to continue, the readjustment of equilibrium will go on until all the H_2SO_3 is decomposed, when, of course, no more action is possible. From this we may say, generally, that a reaction will proceed to completion when one of its products is a gas which is allowed to escape. The same is true, in reactions in solution, when one of the products separates out in the solid form, is precipitated.

Most, if not all, reactions are to be considered reversible, but the question of reversible reactions and chemical equilibrium is a very complicated one, and larger books must be consulted by those who desire to know more about it.

Sulphur Trioxide, SO_3, sulphuric anhydride.—As has already been said, sulphur dioxide and oxygen will combine to form sulphur trioxide; but, under ordinary conditions, and even at high temperatures, this reaction is extremely slow. There are certain substances, however, whose mere presence in the mixture of SO_2 and O hurries up the reaction enormously, so that it becomes almost instantaneous. The best substance for this purpose is very finely divided platinum, platinum black (generally deposited on asbestos), though certain metallic oxides, such as iron oxide, have also been found efficient. Substances which act in the way just described, *i.e.*, by hurrying up a reaction that would, however, go of itself, though much more slowly, are called catalysers, or catalytic agents, and the action itself is called catalysis. (The products in the presence of the catalyser are just the same as they would be without it—they are merely formed more rapidly.)

A Catalyser *is a substance which influences the velocity of a reaction.*

We have already had an excellent example of a catalyser in the case of MnO_2, which accelerates the decomposition of $KClO_3$ and of H_2O_2 to such a remarkable extent.

There are negative as well as positive catalysers, *i.e.*, substances which decrease the velocity of a reaction. Thus, ordinary hydrogen peroxide solution decomposes with a very noticeable rapidity; if a very small quantity of acetanilide (or certain other substances) be added to it, the decomposition is so much slowed down that it is practically stopped altogether.

Sulphur trioxide then may be prepared by passing a mixture of SO_2 and air (or oxygen) through a tube loosely packed with platinised asbestos, and kept at a temperature of about 400°. It is a colorless liquid which freezes at about 15° and boils at about 46°. It vaporises to a considerable extent at ordinary temperatures and it fumes strongly in the air. It combines with water with liberation of so much heat that a hissing sound is produced and sulphuric acid is formed ; SO_3 is therefore sulphuric anhydride, the anhydride of sulphuric acid.

If the ordinary sulphur trioxide be kept for some time at a temperature below 25°, especially if a trace of water be present, it slowly changes into S_2O_6, which forms groups of silky needles looking like asbestos. If this form be heated to 50°, it is reconverted into ordinary SO_3.

Sulphuric Acid, H_2SO_4, oil of vitriol.—This is one of the most important chemicals manufactured, there being but very few trades that do not use it or some of its products.

Basil Valentine, a Benedictine monk of Southern Germany, who lived in the second half of the fifteenth century, clearly describes the preparation of the acid by distilling green vitriol (iron sulphate), whence its name of oil of vitriol, and it was probably known before his time. The manufacture of the acid, by a different method, was introduced into England about 1740 and has developed to such an extent that over one million tons are produced annually in Great Britain, about the same amount in Germany and also in the United States, and smaller quantities in other countries.

There are two processes by which sulphuric acid is manufactured commercially, the older, or chamber, process and the more modern, contact process. In both processes, SO_2 is prepared by burning sulphur or by roasting sulphides, as has already been described.

(1) *Chamber Process.*—This was the method by which almost all the sulphuric acid of commerce was made, from about 1750 to about 1900, since which date enormous quantities have also been made by the contact process. In the chamber

process, SO_2,O (from the air) and H_2O (as steam) are introduced into enormous lead-lined chambers, measuring often 100 × 40 × 20 feet; and here they combine to form H_2SO_4. Unfortunately they will do this by themselves only with extreme slowness, hence a catalytic agent is used—an oxide of nitrogen, obtained from nitric acid. There is still a good deal of uncertainty among chemists as to just what takes place in the chambers—probably different reactions take place in different parts where the temperatures are different. About the simplest set of equations that has been proposed to represent the reactions are the following:

$$2SO_2 + 2HNO_3 + H_2O = 2H_2SO_4 + N_2O_3$$
$$2SO_2 + H_2O + N_2O_3 + 2O = 2SO_2(OH)ONO$$
$$2SO_2(OH)ONO + H_2O = 2SO_2(OH)(OH) + N_2O_3$$

In actual practice the sulphur or the sulphide is burned in burners and the gases produced, containing SO_2 and air, very hot, are made to take up vapor of nitric acid as they pass along a channel. They are introduced into a tower,

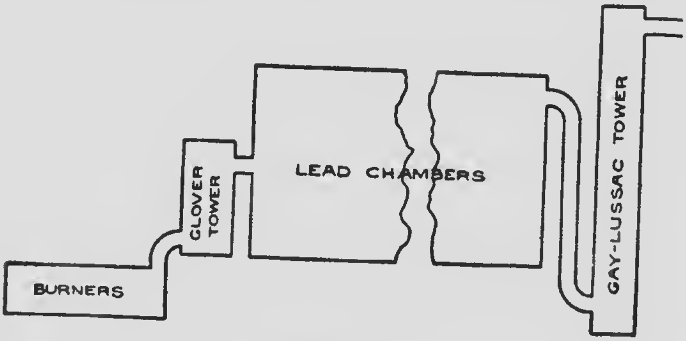


FIG. 15.

called a Glover tower, where the above reactions take place in part, and then they go on to the lead chambers. Here the main production of acid takes place, steam being introduced and the reactions mentioned above being completed, dilute sulphuric acid, called chamber acid, collecting on the floors. The waste gases, mainly atmospheric nitrogen with a little N_2O_3, then pass through another tower called the Gay-Lussac tower, where most of the N_2O_3 is caught and returned to the process. (Theoretically, any small quantity of N_2O_3 would be sufficient to produce any large quantity of sulphuric acid, as it is continually being regenerated. In practice, however, there are unavoidable losses, so there must be a continual though small addition of nitric acid.) The chamber acid is concentrated in order to get rid of the excess of water which it contains.

(2) *Contact Process.*—This was introduced about 1900 and is much simpler in principle than the chamber process, only two reactions being involved after the SO_2 is produced :

$$SO_2 + O = SO_3$$
$$SO_3 + H_2O = H_2SO_4$$

Great care, however, is needed in order that the process should work successfully. The mixture of SO_2 and air from the burners or roasters must be freed from every trace of dust and other impurity; it is then passed through iron tubes containing the catalyser (platinum black, iron oxide, etc.) and kept at exactly the right temperature. The resulting SO_3, mixed with a great deal of nitrogen and some oxygen, is absorbed in water (or better, in dilute sulphuric [illegible] A very concentrated and pure acid is obtained in [illegible] way. It is impossible to say whether this process [illegible] eventually supersede the old chamber process, or not. At present, both processes are being carried on successfully on the large scale.

Sulphuric acid is a colorless, odorless, oily liquid, nearly twice as heavy as water. It boils at about 330°. The strong acid is an oxidising agent, breaking down into SO_2, H_2O and O, especially when there is anything present which will combine with the O (see prep. of SO_2, p. 114).

In aqueous solution it reacts with many of the metals, hydrogen being given off and a sulphate of the metal being formed:

$$Zn + H_2SO_4 = 2H + ZnSO_4$$

This is what might be called the typical reaction between an acid and a metal. It also reacts metathetically with salts of other acids, liberating these acids:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

This is one of the commonest methods of obtaining acids—by acting on their salts with a "stronger" acid.

Concentrated sulphuric acid has a very strong affinity for water, and when the two are mixed, much heat is produced; indeed, the heat is sometimes sufficient to cause the solution to boil and splash out of the vessel. Hence, great care should be taken in bringing these two substances together, the acid being slowly added to the water with constant stirring, and not *vice versa*. Strong sulphuric acid will often extract water from substances which hold it in combination, charring them if they are organic. Thus, if it be slowly poured into a strong solution of sugar, stirring meanwhile, the mixture finally turns black from liberated carbon and swells up, becoming very hot from the chemical action. (Sugar is $C_{12}H_{22}O_{11}$.)

Salts of sulphuric acid are called sulphates.

It will be remembered that, in the definition of an acid, it was stated that the hydrogen was replaceable. (Sometimes only part of it is replaceable.) In the case of hydrochloric acid, which contains only one atom of hydrogen in the molecule, we must replace all or none of the hydrogen—the only sodium salt possible (Na having a valence of 1) being NaCl. In the case of sulphuric acid, however, we might have one of the H atoms replaced by one Na, or both by two Na, thus: $NaHSO_4$ or Na_2SO_4.

The Basicity of an Acid *is the number of replaceable hydrogen atoms contained in one of its molecules.* An acid containing one atom of replaceable hydrogen in the molecule is called a monobasic acid ; one containing two, dibasic ; three, tribasic ; four, tetrabasic, etc. It must be carefully noticed that it is the number of *replaceable* hydrogen atoms in *one* molecule of the acid that determines its basicity : $HC_2H_3O_2$ is acetic acid, the acid of vinegar ; it is monobasic, because only one of the hydrogen atoms is replaceable, the others are not. Moreover, two molecules of HCl contain two replaceable hydrogen atoms, but this does not make the acid dibasic.

A Normal Salt *is one in which all the replaceable hydrogen of the acid (from which the salt is theoretically derived) has been replaced,* such as NaCl, or Na_2SO_4.

An Acid Salt *is one in which only part of the replaceable hydrogen of the acid has been replaced,* such as $NaHSO_4$. Monobasic acids cannot, of course, produce acid salts.

Of the several million tons of sulphuric acid annually produced in the whole world, a large proportion is used in the manufacture of soda (see Leblanc process, p. 197) ; enormous quantities are employed in preparing fertilisers ("superphosphate") ; in refining petroleum and in "pickling" (*i.e.*, cleaning) iron and steel before plating with tin, copper, or nickel ; and smaller quantities in the manufacture of other acids and in various other industries.

Thiosulphuric Acid, $H_2S_2O_3$.—The Greek name for sulphur is *thion*; thiosulphuric acid, then, is sulphur-sulphuric acid, *i.e.*, sulphuric acid in which one oxygen has been replaced by a sulphur, H_2SSO_3. It was formerly called hyposulphurous acid, and its sodium salt, sodium hyposulphite, or "hypo." This compound is used in photography and as an "antichlor" in bleaching, to prevent the excess of chlorine doing the material itself any harm after the color has been destroyed.

Selenium and **tellurium** are two rather rare elements, closely related to sulphur. Selenium is of interest because its electric conductivity is affected by light, and, on this account, it is used in certain electrical instruments.

QUESTIONS

1. Define the term anhydride. How many classes of anhydrides are there? Mention two members of one of these classes and point out why they are called anhydrides.

2. Show how the two oxides of sulphur illustrate the law of multiple proportions.

3. Oxygen and sulphur belong to the same family of elements; in what ways are they similar? Are physical or chemical likenesses the more important in classifying the elements?

4. Wooden shelves on which bottles containing sulphuric acid are stood often become more or less burned in rings corresponding to the bottoms of the bottles. Explain this.

5. Why are there no acid salts of monobasic acids?

6. What catalyser is used in the chamber process for the manufacture of sulphuric acid? What in the contact process? Why are they employed?

7. Can you suggest a method for distinguishing "fool's gold" from real gold?

8. Do you think that a mixture of H_2S and air would be explosive? Why?

9. H_2S is soluble in water, and yet we collect it over water in the pneumatic trough. Explain.

10. Write an equation showing that sulphuric acid sometimes acts as an oxidising agent.

11. Why are SO_2 and SO_3 called anhydrides? Why is SO_2 called sulphur*ous* anhydride?

12. A sulphuric acid plant is often connected with a copper smelter. Why do you think this is so?

13. Compare, in tabular form, the properties of rhombic and of monoclinic sulphur.

14. What does 22.4 litres sulphurous anhydride weigh? Why do you think so? What is its density, compared with that of air?

15. How much sulphuric acid can be obtained from a ton of pyrite?

16. 10 gr. of $CuCl_2$ is dissolved in water. What quantity of sulphuric acid and of ferrous sulphide is necessary to produce enough H_2S to precipitate the copper as CuS?

$$CuCl_2 + H_2S = CuS + 2HCl$$

CHAPTER XII

NITROGEN. THE ATMOSPHERE COMPOUNDS OF NITROGEN

History.—The last quarter of the eighteenth century was a most remarkable period in the history of chemistry. As we have already seen, all through the middle ages people believed in "the four elements of Aristotle," earth, air, fire and water. Earth was the first of these whose elementary nature was doubted; and then, in 1774, Priestley discovered oxygen, which turned out to be one constituent of air (which could therefore no longer be looked upon as an element) and which helped to explain the nature of fire; in 1781 Cavendish showed the compound nature of water; and even before these two discoveries, *i.e.*, in 1772, the Scotch botanist, Rutherford, showed that air was made up of two or more gases, one of which he isolated and studied—it is the gas we now know as nitrogen. Earth, air, fire and water, the elementary nature of every one of them disproved; and, in addition, a far-reaching theory concerning combustion (the phlogiston theory) overthrown and replaced by a new and well-founded one: is it any wonder that the profound change in chemical ideas which took place at this period is often spoken of as "the Chemical Revolution"? What a modern thing scientific chemistry really is!

Occurrence.—As has already been indicated, nitrogen occurs in the air of which it forms about four-fifths by volume; it also occurs in combination in nitre, or saltpeter, KNO_3, in Chili nitre, $NaNO_3$, and in the living parts of all plants and animals, it being an essential constituent of protoplasm (albumen, etc.). It occurs in combination in coal, fossil vegetable matter, which is the principal commercial source of some of its compounds, as we shall see later.

Preparation.—For ordinary purposes, nitrogen can be obtained from the air by extracting the oxygen. This may be done in many ways, differing mainly in convenience; phosphorus is the agent generally employed because (1) it extracts the oxygen very completely and (2) the oxide formed is rapidly absorbed by water and removed from the nitrogen.

EXPERIMENT.—The cover of a porcelain crucible, or some other small dish, is placed on a large flat cork and floated on some water in a pan. A piece of phosphorus the size of a pea is placed in the little dish and is ignited by bringing a hot wire in contact with it, and immediately a bell-jar or inverted bottle is placed over it. What happens? What experiment taught us the composition of the white substance formed? What takes place on standing? What portion of the original air is left in the bell-jar at the close of the experiment? How do we know (without further test) that it does not burn or support combustion? Is it very soluble in water? How do we know?

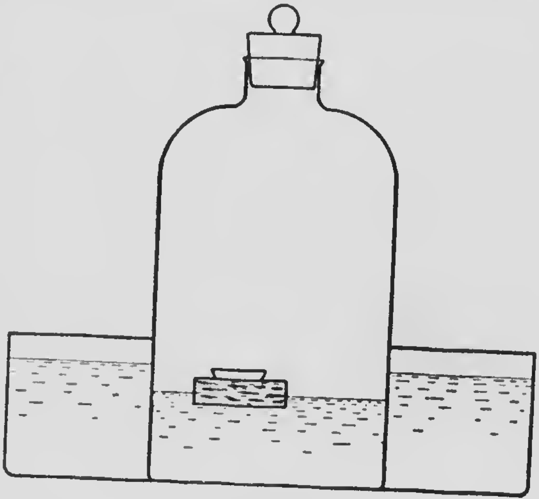


FIG. 16.

The oxygen may also be removed by passing the air over red hot copper in a tube, as it combines with the copper to form solid copper oxide, which remains in the tube while the nitrogen passes on.

The gas obtained by the methods given above is often spoken of as "atmospheric nitrogen" and is not quite pure, as the air contains a little over 1% of gases other than the nitrogen, which are not removed with the oxygen. Their presence in the nitrogen, however, does not matter as far as we are concerned here.

As we shall learn later, nitrogen is not chemically combined with anything in the air. For certain reasons, it is sometimes interesting to get it from substances in which it exists in combination, and this can be done in many ways; but perhaps it is most easily accomplished by heating a solution of ammonium nitrite,

$$NH_4NO_2 = 2H_2O + 2N$$

With proper precautions this yields chemically pure nitrogen. Nitrogen obtained from compounds is often spoken of as "chemical nitrogen."

Properties.—Like oxygen and hydrogen, nitrogen is a gas, colorless, odorless and tasteless. It is slightly lighter than air, the G.M.V. weighing 28 gr. (G.M.V. of air = 28.8 gr.). It is only very slightly soluble in water, 100 volumes of the latter dissolving about 1.5 volumes of nitrogen.

Its boiling point is -195° and its melting point -214°. As a liquid it is colorless; the solid is a colorless crystalline mass.

The chemical properties of nitrogen are mostly negative—it does not burn or support combustion or respiration. It is not poisonous (we breathe it all the time). At high temperatures it combines with a few substances, *e.g.*, magnesium, with which it forms the nitride, Mg_3N_2.

If the product of combustion in experiment (p. 18) be moistened with water, the odor of ammonia will be noticed, a little Mg_3N_2 having been formed along with the MgO when the magnesium burned in the air. This compound is decomposed by water, as follows:

$$Mg_3N_2 + 6H_2O = 2NH_3 + 3Mg(OH)_2$$

When electric sparks are passed through air, the following combination takes place just along their path, and exactly the same thing happens in an electric arc in the air:

$$N + 2O = NO_2$$

The Atmosphere.—As has already been intimated, a correct knowledge of the chemistry of the atmosphere has been obtained only at a comparatively recent date. One of the very first men to notice that air was not all one substance was the Scotch chemist, Joseph Black, who (in 1755) pointed out that it contains a small proportion of "fixed air" (carbon dioxide). Then in 1772, as we have already learned, Rutherford, who was a pupil of Black's, discovered its nitrogen; in 1774 Priestley discovered oxygen and showed that it, too, was a constituent of air. The presence of water vapor in the atmosphere had been known for a long time, and minute quantities of ammonia, nitric acid and some other substances have also been recognised in it.

One would have thought, after all that had been learned about gases at the end of the eighteenth century and since, that the exact composition of the atmosphere would have been finally settled almost a century ago. But such, however, was not the case, and one of the most brilliant chapters in modern chemistry is connected with this very subject.

In 1893 the English physicist, Lord Rayleigh, noticed that "atmospheric nitrogen" was slightly heavier than "chemical nitrogen." Using a certain bulb, he found in several experiments that the weights of nitrogen which it held (reduced to standard temperature and pressure) were as follows:

Atmospheric nitrogen	2.3103 gr.	Chemical nitrogen	2.3001 gr.
"	2.3100 "	"	2.2990 "
"	2.3102 "	"	2.2987 "
		"	2.2999 "

As the results for atmospheric nitrogen agreed very well among themselves, as did also those for chemical nitrogen, but as the results for the former differed from those for the latter by much more than the experimental error, it was necessary to find the cause. Lord Rayleigh invited Professor (now Sir William) Ramsay to join him in the investigation, and in 1894 they announced the discovery of a new constituent of the atmosphere, which they called argon; and Ramsay styled the discovery "the triumph of the last decimal place."

Composition of the Atmosphere.—The proportion of *water vapor* in the air varies very much with time and place, its maximum under ordinary conditions being about 1% by weight and its minimum about 0.1%. The *carbon dioxide* varies from about 0.046% by weight in country air to double that amount in city air, and up to as much as 0.76% in crowded audience rooms. It is most probable that such a high proportion of carbon dioxide in air is in itself quite harmless, but it is generally accompanied by other impurities, products of respiration, which are distinctly harmful. The atmosphere as a whole is, of course, enormous in quantity, and the changes in composition due to various local causes are quickly readjusted by diffusion assisted by wind.

Carbon dioxide is constantly being produced in processes of combustion, respiration and decay, and from volcanoes, geysers, etc. But at the same time it is being withdrawn by plants, forming as it does the principal article of their food. In this way, the proportion in the atmosphere as a whole remains stationary.

The relative quantities of *oxygen* and *nitrogen* in air have been determined with extreme accuracy, the general principle of one of the methods being illustrated in the experiment already described of preparing nitrogen from air. If this experiment be carried out by passing a piece of phosphorus up into a graduated tube full of air over water, and the phosphorus be allowed to combine very slowly with the oxygen (without actual quick burning), the result is of course more exact than when the experiment is performed as described above. The general results of the most accurate analyses performed by this and other methods are:

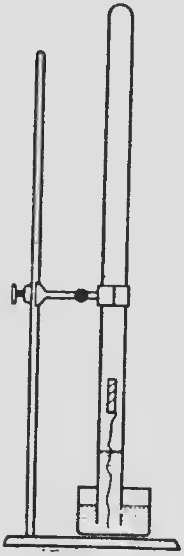


FIG. 17.

	VOLUME	WEIGHT
Oxygen	20.96%	22.92%
Nitrogen	79.04	77.08

but with positive evidence of very slight variations from time to time and in different places. So nearly constant is the proportion of oxygen to nitrogen in air, that the question naturally arises: are we dealing with a chemical compound or with a gaseous solution? There are many reasons for believing that air is *not* a compound, among them being the following:

1. When oxygen and nitrogen are brought together in the proportions in which they exist in air (*a*) there is no change in temperature, no contraction, or other sign of chemical combination; and (*b*) the solution (mixture) has all the essential properties of pure air.

2. The relative quantities of oxygen and nitrogen in air are not absolutely constant, as would be the case if air were a compound (*cf.* law of definite proportions).

3. The ratio of oxygen to nitrogen bears no simple relation to the ratio of their atomic weights.

$N_{50}O_{13}$ represents the proportions pretty well, but indicates a molecular weight of 908, whereas the weight of 22.4 litres of air is about 28.8 gr.

4. A liquid which is a definite chemical compound has a definite boiling point. As liquid air boils, its temperature slowly rises, most of the nitrogen boiling off first with only a little oxygen, leaving oxygen with only a little nitrogen. (Compare separation of alcohol and water by distillation, p. 173.)

5. The properties of air are the means of those of its constituents, proper regard being paid to their proportions.

Hence, air is to be regarded, not as a compound, but as a (gaseous) solution. (It was formerly spoken of as a mixture, but this is now considered an incorrect use of the term.)

Properties.—As has already been said, the properties of air lie between those of its constituents, remembering always that there is about four times as much nitrogen present as oxygen. Thus: oxygen, nitrogen and air are gaseous, colorless, odorless and tasteless; 22.4 litres of oxygen weighs 32 gr., of nitrogen 28 gr. and of air 28.8 gr. Nitrogen does not support combustion at all, oxygen with great energy, and air with less energy. Most of the chemical properties of air are due to its content of oxygen; thus, it supports combustion, *the same products being formed as are produced when the combustion takes place in oxygen.* (This is one of the principal proofs of the presence of oxygen in air, because gases other than oxygen support combustion but do not produce oxides. The reasoning may be put in mathematical form, thus :

$$\text{Substance} + X = \text{oxide of substance.}$$

Knowing two of the three terms of the equation we can, of course, find the third.) Air not only supports combustion (including many kinds of slow combustion, such as decay) but it also supports respiration. The nitrogen in the air serves to dilute the oxygen and thus moderate the processes of combustion and respiration ; it also is an important constituent of the food of certain plants.

While most plants are unable to make use of free nitrogen as a constituent of their food, it has long been known that the leguminosæ (clover, peas, beans, etc.) could do so. It has been found that this is due to the co-operation of certain microscopic bacteria living in little nodules on their roots. Certain other plants also seem to be able to assimilate atmospheric nitrogen, though how they do it is not understood. Most plants are incapable of doing it.

The carbon dioxide in the air is an essential food of plants; and water vapor prevents evaporation going on too rapidly from plants and animals, and also, on condensation, forms rain, without which most vegetation would perish and we should have no streams.

The minute quantities of ammonia, nitric acid, etc., when washed into the soil by rain, are valuable fertilisers. Argon and the other members of its family have no use, so far as is known.

Besides the substances already mentioned, air contains vapors of various kinds derived from factories, etc., and dust from many sources. The dust is irritating to the breathing passages and is liable to contain disease germs and then becomes very dangerous.

Argon was discovered by Rayleigh and Ramsay in 1894. "Atmospheric nitrogen" was passed back and forth over heated magnesium turnings in a tube till all the nitrogen had combined to form Mg_3N_2, and the gas which was left over, about 1% of the "atmospheric nitrogen," was called argon. Another method of removing the nitrogen is to add oxygen to air and pass electric sparks; NO_2 is slowly formed and is absorbed in a solution of KOH. Argon resembles nitrogen very closely in physical properties but is a little heavier, tho G.M.V. weighing about 40 gr. It seems, however, to have absolutely no power of combining with anything, even its molecule has been proved to consist of only one atom—hence its name, from a Greek word meaning *idle*.

The argon obtained from the air is found to be not quite pure, and small quantities of four other gases have been separated from it: helium, neon, krypton and xenon, their names being derived from Greek words meaning, respectively, the *sun, new, hidden, stranger*. Curiously enough, helium had been discovered spectroscopically in 1868 in the sun (hence its name) but was not known on this earth till 1895. The proportions in which these gases are found in air are approximately as follows:

Helium .	1-2	vols.	in	1,000,000	vols.	of	air
Neon . .	1-2	"	"	100,000	"	"	"
Argon . .	1	"	"	100	"	"	"
Krypton .	1	"	"	1,000,000	"	"	"
Xenon .	1	"	"	20,000,000	"	"	"

No compounds of any of these elements are known; their atoms seem to have zero valence, *i.e.*, no power whatever of entering into combination, and, in harmony with this, their molecules are found to be monatomic.

Compounds of Nitrogen.—Nearly all animal and a great many vegetable substances contain nitrogen. Coal is fossil vegetable matter. If animal and vegetable matter be heated where air cannot get at it (destructively distilled), it is decomposed and some of its nitrogen is given off in the form of ammonia, NH_3. A great deal of ammonia is produced in this way at the gas works. When animal and vegetable substances decay, the changes that take place are due mainly to the growth of different kinds of microscopic living things called bacteria. Some of these will grow where there is little or no air, and then the nitrogen is converted mainly into ammonia, as was the case during destructive distillation. (Sometimes the interior of large and old piles of manure smells strongly of ammonia.) If the decay takes place where there is plenty of air, then other kinds of bacteria convert the nitrogen into nitric acid, HNO_3, which combines with bases present, such as potash and lime, to form the corresponding nitrates, KNO_3, $Ca(NO_3)_2$.

Some plants growing along the sea shore contain mainly soda in place of the potash found in ordinary land plants, and when they decay under proper conditions, $NaNO_3$ is formed. This is supposed to be the origin of the deposits of Chili saltpeter, $NaNO_3$, huge accumulations of sea weed having been lifted out of the ocean by the rising of the western coast of South America, and these having decayed, the sodium nitrate was leached out of them and deposited in a valley.

Ammonia and nitric acid are the two sources from which most of the other compounds of nitrogen are produced.

Ammonia, NH_3.—It is an exceedingly tedious and expensive process to prepare ammonia from its elements; but, as has already been said, it may be produced (along with a lot of other substances) by subjecting organic matter containing nitrogen to destructive distillation. In the old days they used to distil the horns of a kind of deer, called a hart, for this purpose, and called the ammonia obtained "spirits of hartshorn." Nearly all the ammonia of commerce is now obtained as a by-product in the manufacture of coal gas. When the coal is distilled, a great many volatile substances are given off, some of which condense (tar) and some do not. The ammonia is one of these latter and is separated from the coal gas by passing the whole through water, when the ammonia is dissolved and the rest passes on. Much of this dissolved ammonia is then converted into ammonium chloride or ammonium sulphate by causing it to combine with hydrochloric or sulphuric acid. In the laboratory, ammonia is prepared by bringing together ammonium chloride (salammoniac) and a strong base, such as sodium hydroxide (caustic soda), the reaction being a metathetical one.

$$NH_4Cl + NaOH = NaCl + NH_4OH$$

and then the NH_4OH, being a very unstable compound, breaks down

$$NH_4OH = NH_3 + H_2O$$

If quicklime be used instead of caustic soda, the reaction is

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

Experiment.—Mix about 10 gr. solid ammonium chloride with an equal quantity of quicklime and place the mixture in a hard-glass test-tube fitted with a delivery tube, as in the figure. Hold a bottle over the delivery tube and heat the test-tube and its contents. The ammonia produced collects at the top of the bottle, forcing the air down and out. Why? This is called collecting by upward displacement. Test the gas with a lighted match. What is the result? Turn the delivery tube down into a beaker with a little water in it, so that the opening of the tube is just above the surface of the water. Why? Continue heating. Test the water with red litmus and also notice its odor. Is NH_3 soluble in water?

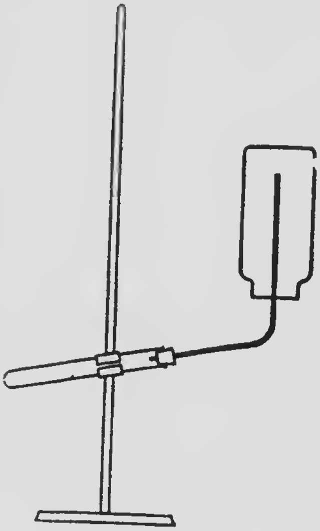


Fig. 18.

From the experiment described above, we see that ammonia is a gas, colorless, with a strong characteristic odor (and taste). The G.M.V. weighs 17 gr. (and is recorded in the formula NH_3, $14 + 3 = 17$); therefore the gas is about half as heavy as air. It is easily condensed to a liquid, and is also very soluble in water, 1 volume of the latter dissolving about 1,000 volumes of the gas under ordinary conditions. The solution, which is what we generally buy as ammonia, is called aqua ammonia or liquor ammoniæ. Ammonia does not support combustion, nor will it burn (except in pure oxygen, and then only with a feeble flame).

Ammonia is used for various purposes. The liquefied substance volatilises very easily and all liquids absorb much heat in so doing; hence, liquid ammonia is much used in refrigerating machines. The gas is used in making soda by the Solvay process (see p. 198), and the solution (ammonia) is used for cleaning purposes in the household, as it removes grease (forming with it a sort of soap).

Ammonium Hydroxide, NH_4OH.—When ammonia dissolves in water a solution is produced that has a strong basic or alkaline reaction, *i.e.*, turns red litmus blue. Now, the compounds that do this, bases, contain the group OH, hydroxyl (see p. 104); hence, some hydroxyl compound must have been produced by the reaction between NH_3 and H_2O. The simplest reaction that could have brought this about is

$$NH_3 + H_2O = NH_4OH$$

and we call the substance ammonium hydroxide. With acids, it reacts in just the same way that sodium hydroxide does (see p. 105).

$$NH_4OH + HCl = NH_4Cl + HOH$$

We see that the group NH_4, which is called ammonium, plays the same part as the metal Na does; on this account it is called a *compound metallic radical.* It has a valence of 1. We shall see later more of its resemblance to a metal.

Nitric Acid, HNO_3.—This substance was known to the alchemists and, on account of its great activity, was called by them *aqua fortis,* powerful water, or liquid.

Potassium nitrate, KNO_3 (nitre, or saltpeter), and sodium nitrate, $NaNO_3$ (Chili nitre or Chili saltpeter), are both found in nature, and by acting on them with sulphuric acid, nitric acid is obtained:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$
$$\text{and } NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3$$

(One of the reasons for applying the term "acid salt" to $NaHSO_4$ is apparent from the above reactions—it acts like an acid.)

EXPERIMENT.—Put about 20 gr. potassium nitrate into a retort, place a thistle tube in the neck of the retort and pour in enough concentrated sulphuric acid to cover the salt. (Do not allow any acid to run down the neck of the retort.) Slip a small flask or wide test-tube over the neck of the retort and set up the apparatus, clamped to the retort stand, near the sink, so that the receiving vessel is directly under the water tap. Heat the retort with a small flame and keep the receiver well cooled by running water over it. Note the color of the distillate. Define distillate. Why is it not clear like the nitric acid in the bottles? The brown vapor evolved in the distilling flask is not the vapor of nitric acid. What is it and what produced it? (See below.)

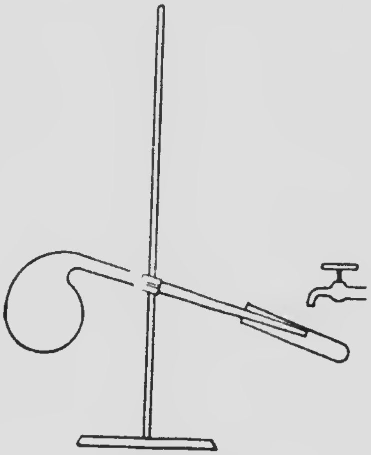


FIG. 19.

Nitric acid is prepared commercially in enormous quantities and is used in the manufacture of explosives, dyes, etc.

It is a colorless liquid, when pure, with a peculiar choking odor. It boils at 86° (Sp. gr., 1.56). When exposed to sunlight or when heated, some of it decomposes according to the equation

$$2HNO_3 = H_2O + 2NO_2 + O$$

The NO_2, nitrogen peroxide, is a brownish gas which is readily soluble in nitric acid; hence, nitric acid which has been exposed for some time to the light, or which has been heated, has a yellowish or brownish color. The "concentrated" commercial acid is 68% HNO_3 and 32% H_2O and boils at 120.5° (Sp. gr., 1.4). On account of the ease with which the acid breaks up, yielding oxygen, and also because NO_2 easily gives up half its oxygen if there is anything to combine with it, nitric acid is a powerful oxidising agent. A point of glowing charcoal introduced into pure (water-free) nitric acid will continue to burn.

Nitric acid is a strong acid as well as a powerful oxidising agent. Most metals react vigorously with it, the corresponding nitrates being formed.

$$Ag + HNO_3 = AgNO_3 + H$$
$$Cu + 2HNO_3 = Cu(NO_3)_2 + 2H$$

Gold and platinum are not attacked, and tin and antimony are converted into insoluble hydrated oxides, not soluble nitrates. Under ordinary conditions, no hydrogen is liberated in these reactions; this is because of the strong oxidising action of the nitric acid, the hydrogen being oxidised to water, the reaction generally being the following:

$$HNO_3 + 3H = 2H_2O + NO$$

If we combine this equation with, for instance, the one just given for the reaction for copper, we get

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

If nitric and hydrochloric acids be mixed, the nitric acid oxidises the hydrogen of the hydrochloric acid to water, some of the chlorine being liberated and the rest combining with NO from the nitric acid:

$$HNO_3 + 3HCl = 2H_2O + 2Cl + NOCl$$

Now, free chlorine will attack gold and platinum, producing chlorides which are soluble. Hence, if a mixture of nitric and hydrochloric acids be poured on gold or platinum, the metal is slowly dissolved. Gold used to be called *rex*, the king of metals; and this mixture of acids was called *aqua regia*, royal water or liquid, because it would dissolve rex, the king of metals.

Nitric acid acts violently on the flesh and on clothing; therefore great care must be taken in handling it.

Nitrous Acid.—Nitrates undergo decomposition when heated, different degrees of breaking down taking place in different cases. If sodium nitrate be carefully heated, the following reaction takes place:

$$NaNO_3 = NaNO_2 + O$$

If the $NaNO_2$, sodium nitrite, be treated with very dilute sulphuric acid, a solution of *nitrous acid*, HNO_2, is obtained. This is a very unstable acid, breaking down easily into its anhydride, N_2O_3 and water.

Oxides of Nitrogen.—Nitrogen combines with oxygen in five different proportions, to form five different oxides.

N_2O	Nitrous oxide
(N_2O_2) NO	Nitric oxide
N_2O_3	Nitrous anhydride
(N_2O_4) NO_2	Nitrogen peroxide
N_2O_5	Nitric anhydride

We may use this series of oxides to show in a striking manner the use of theories in saving mental labor. If we analyse these oxides we get their composition as follows:

	NITROGEN	OXYGEN
Nitrous oxide	63.71%	36.29%
Nitric oxide	46.75	53.25
Nitrous anhydride	36.91	63.09
Nitrogen peroxide	30.51	69.49
Nitric anhydride	25.99	74.01

Now, what a task it would be to commit all these numbers to memory. On the other hand how easy it is to remember the above list of formulas; and then, by also remembering that $N = 14$ and $O = 16$, how simple to calculate the proportions of the constituents of the different compounds when we want them.

Moreover, the list of percentages does not exhibit any striking relationships among the compounds, as the formulas do. It would take a lot of thinking to arrive at the law of multiple proportions from the composition of these compounds when expressed in percentages, but when expressed in formulas, it "strikes one in the eye." Indeed, these oxides of nitrogen form one of the best illustrations which we have of the law of multiple proportions, because (*using the formulas as an aid to memory*) 28 parts by weight of nitrogen combines respectively with 16, 32, 48, 64, 80 parts by weight of oxygen, and these numbers, 16, 32, 48, 64, 80 bear very simple ratios to each other *i.e.*, 1:2:3:4:5. We must remember, in this connection, that the law of multiple proportions preceded the atomic theory and it, the *law*, has nothing to say about atoms. Hence, it would be incorrect to state that these oxides of nitrogen illustrate the law because 1, 2, 3, etc., *atoms* of oxygen are respectively combined with 2 *atoms* of nitrogen. We must confine ourselves to *quantities*, or *parts by weight*, when discussing the law and the compounds that illustrate it. We must also keep in mind that the oxides of nitrogen do not have certain compositions because such and such are their formulas; but these are their formulas because the oxides have been found to have certain compositions. This, however, being thoroughly understood, we may commit the formulas or the compositions to memory, whichever we find the easier, knowing that we can calculate the other one when we want it.

Nitrous oxide, N_2O, laughing gas.—This gas was one of Priestley's numerous discoveries, and it is prepared by carefully heating ammonium nitrate and collecting the gas over hot water:

$$NH_4NO_3 = 2H_2O + N_2O$$

It is a colorless gas with a slight pleasant odor and sweetish taste. It is comparatively easily liquefied by pressure and is sold in this condition in steel cylinders. It is moderately soluble in cold water, but, like all gases, less so in hot water. If substances which burn in oxygen be highly heated and introduced into nitrous oxide, it supports combustion as well as oxygen does, oxides being formed and nitrogen set free. When breathed in diluted form it causes a sort of intoxication accompanied by hysterical laughter—hence its common name; when inhaled pure it causes insensibility and on this account is used in surgical operations, particularly in the extraction of teeth. (Great care must be used in seeing that the gas contains no harmful impurities if it is to be breathed.) It will not support respiration, so continued breathing of it, to the exclusion of air, would produce death.

Nitric oxide, NO, is prepared by bringing together nitric acid of ordinary strength (68%) and copper:

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

It is a colorless gas, only very slightly soluble in water. It does not burn or support combustion. When brought into contact with oxygen it unites with it at once, forming reddish-brown nitrogen peroxide, which is readily soluble in water.

$$NO + O = NO_2$$

Nitrous anhydride, N_2O_3, is, as its name indicates, the anhydride of nitrous acid,

$$H_2O + N_2O_3 = 2HNO_2$$

Nitrogen peroxide, NO_2, is formed from nitric oxide and oxygen, as indicated above. It is also slowly produced when electric sparks are passed through a mixture of oxygen and nitrogen. It is a reddish-brown gas of disagreeable odor and is poisonous when inhaled in any quantity. It dissolves easily in water, with which it reacts, forming nitrous and nitric acids:

$$2NO_2 + H_2O = HNO_2 + HNO_3$$

As has already been stated, nitrogen compounds form an essential constituent of the food of plants; they are among the first that cultivated soil becomes poor in and are expensive to replace. Hence the economic manufacture of some sort of fertiliser that contains these compounds is an exceedingly important problem, and is rapidly becoming more and more pressing, as the natural sources of such compounds are strictly limited. Of late years many endeavors have been made to prepare nitrogen compounds from the air, and one method is now being successfully applied in Norway, where water power is very cheap. This consists in passing electric sparks through air and absorbing the NO_2 thus produced in a solution of slaked lime:

$$4NO_2 + 2Ca(OH)_2 = Ca(NO_2)_2 + Ca(NO_3)_2 + 2H_2O$$

The mixture of calcium nitrite and calcium nitrate thus obtained can be applied directly to the soil as a fertiliser.

Nitric anhydride, N_2O_5, may be prepared by extracting water from nitric acid by means of powerful dehydrating agents:

$$2HNO_3 - H_2O = N_2O_5$$

This action can be reversed, the anhydride combining with water to form acid.

QUESTIONS

1. Why do you think we speak of the "Chemical Revolution" of the eighteenth century?

2. Some author has used the phrase "No life without nitrogen." To what do you think he referred? Do you consider the phrase very accurate? Why?

3. Can ammonia be collected over the pneumatic trough in the ordinary way? What modification would render this method of collection possible? Would this work in the case of chlorine?

4. How could you prove that air contains (*a*) oxygen, (*b*) nitrogen, (*c*) carbon dioxide, (*d*) water vapor?

5. How does a chemical compound, *e.g.*, of nitrogen and oxygen, differ from a (gaseous) solution of these two substances?

6. What chemical action do you think might take place in air during a thunder storm?

7. Why does the composition of the air remain so nearly constant?

8. Several gases besides oxygen support combustion. How do we know that the air contains oxygen?

9. Why do you think that ammonia is sometimes called the volatile alkali? Why, spirits of hartshorn?

10. Show how the oxides of nitrogen illustrate the law of multiple proportions. How are their formulas to be used in this connection?

11. How may nitrous oxide be distinguished from oxygen?

12. How are ammonia, nitric acid, nitrous acid, and nitrates formed in nature?

13. Why is the "fixation" (*i.e.*, causing to combine) of atmospheric nitrogen an important problem?

14. When oxygen and nitrogen are mixed, no heat is produced. What do we infer from this?

15. Can you suggest a method for the determination of the proportion of water vapor in air?

16. Perfectly dry ammonia has no effect on dry litmus. Why do you think this is so?

17. What weights of sodium nitrate and of sulphuric acid are necessary to prepare one litre of commercial nitric acid?

18. Write the equation that represents the reaction that takes place when a solution of ammonium hydroxide is neutralised with sulphuric acid?

19. Determine the atomic weight of nitrogen from the following data, giving reasons for your procedure:

GASEOUS SUBSTANCE	WT. OF 22.4 LITRES	WT. OF NITROGEN IN 22.4 LITRES
Nitrous oxide	44 gr.	28 gr.
Nitrogen.	28 "	28 "
Nitric oxide	30 "	14 "
Nitrogen peroxide	46 "	14 "
Nitric acid.	63 "	14 "

20. Show from the figures quoted above that nitric oxide and nitrogen peroxide should not be written N_2O_2 and N_2O_4 respectively.

21. What volume of air is necessary for the complete combustion of one ton (1016 kilos) of anthracite coal, containing 88% carbon (the rest being considered as incombustible ash)? $C + 2O = CO_2$.

CHAPTER XIII

PHOSPHORUS. ARSENIC. ANTIMONY. BISMUTH

The elements treated in this chapter are members of the nitrogen family and, as we study them, nitrogen should be kept in mind and the properties of the other elements compared with those of nitrogen as well as with one another.

Phosphorus.—Up to about 1670 all substances that emitted light when cold (like our modern luminous paint) were called phosphorus, the light carrier. (Notice that the noun does not end in *-ous.*) About the date mentioned, a German named Brand discovered the substance which we call phosphorus to-day and exhibited it, but would not tell how he had prepared it. Several people set to work to find out how it was made and two or three succeeded, one of them being Robert Boyle. One of the others wrote a pamphlet about it with a striking title, such as they were fond of in those days: "An open description of Phosphor mirabili and its light-giving wonder-pills."

This element is not found free in nature—when we see how active it is, we are not surprised that it occurs only in combination. Several compounds contain it, such as phosphorite, calcium phosphate, $Ca_3(PO_4)_2$, which occurs not only in a large number of rocks (generally as a closely related but more complex mineral, apatite), but also as the mineral portion of bones (bone ash). All fertile soils contain it (derived from the rocks), as it, or some other compound of phosphorus, is a necessary constituent of the food of plants. Protoplasm, the basis of all plant and animal life, also contains it.

Phosphorus is generally prepared to-day in the electric furnace, a mixture of calcium phosphate, sand and carbon (coke) being slowly and continuously fed in and raised to a very high temperature. (In this connection it should be noticed that sand, SiO_2, is an acid anhydride, $3SiO_2$ being able to replace P_2O_5, another acid anhydride.)

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$$
$$P_2O_5 + 5C = 5CO + 2P$$

At the temperature of the furnace, calcium silicate is a liquid and is tapped off from time to time, and the CO and P are both gases and are conducted under water where the phosphorus condenses, the CO passing off uncondensed. The phosphorus is remelted, purified and cast into sticks.

Phosphorus is an allotropic element, being known in at least two forms: yellow (white) and red phosphorus.

Yellow phosphorus, obtained when phosphorus vapor is condensed, as in the preparation described above, is a pale yellow, translucent, crystalline solid, of a waxy consistency at ordinary temperatures; it can be cut with a knife, and this should always be done under water. It melts at 44° to a yellow liquid and boils at 269°. Its density is 1.9 (water = 1) and it is insoluble in water. (Soluble in carbon disulphide and in some oils.) Yellow phosphorus combines with oxygen slowly at ordinary temperatures and is very apt in so doing to become sufficiently warm to burst into flame, its kindling temperature being 40°. Hence, it is kept under water and extreme care must be used in handling it, as it is so liable to take fire, and burns produced by it are generally very painful and difficult to heal. When it burns it produces P_2O_5. It is very poisonous, even the breathing of its vapor producing an extremely serious disease of the bones (necrosis), generally starting at the jaw and known popularly as "phossy jaw." It is used in rat poisons and in the manufacture of ordinary matches.

Red phosphorus.—Yellow phosphorus changes spontaneously into red phosphorus. This takes place with extreme slowness in the dark at ordinary temperatures, light hastens it, and between 250° and 300° it goes very rapidly even in complete darkness (of course, air must be excluded). Red phosphorus is brownish-red in color, minutely crystalline, odorless and tasteless. Its density is 2.11 and it is insoluble in water, carbon disulphide and oils. It vaporises without melting (400°?). It is unaffected by air at ordinary temperatures, but ignites at 260°. It is not poisonous, and is used in the manufacture of safety matches. It is often very instructive to put information into tabulated form—let us do this with some of the properties of yellow and red phosphorus, as similarities and differences will then appear very strikingly.

	YELLOW PHOSPHORUS	RED PHOSPHORUS
Color	Light yellow	Brownish-red
Specific gravity	1.9	2.11
Melting point	44°	——
Boiling point	269°	400°(?)
Temp. of ignition . . .	40°	260°
In carbon disulphide . .	Soluble	Insoluble
Physiological effect . . .	Poisonous	Not poisonous

Man is distinguished from all other animals by the fact that he uses fire, and this he has done from time immemorial. In very early times fire was exceedingly difficult to produce and was therefore carried long distances and carefully preserved. The oldest way of making fire was by the friction of two pieces of wood. This was followed by striking iron or steel against pyrite or flint, the sparks produced being caught on carefully dried tinder. In 1827 the first lucifer matches were introduced; they consisted of wooden splints the ends of which, after having been dipped in sulphur, were tipped with a mixture of potassium chlorate and sugar. They were ignited by dipping them into a bottle packed with asbestos moistened with fuming sulphuric acid. In the same year, John Walker, of Stockton, England, invented friction matches: wooden splints, with ends dipped in molten sulphur, were tipped with a mixture of antimony sulphide, potassium chlorate and gum; they were ignited by drawing them between two pieces of sand-paper. Yellow phosphorus soon took the place of the antimony sulphide, potassium nitrate that of the potassium chlorate, as the ignition is then less explosive, and wax or paraffin that of the sulphur, as the odor is less disagreeable.

Modern matches are wood splints, having ends soaked in sulphur or paraffin and tipped with a mixture of potassium chlorate, or nitrate, yellow phosphorus and glue. The heat necessary for ignition is obtained by friction of the head on almost any dry surface. As much disease is caused by the yellow phosphorus during manufacture of the matches (and as they are very poisonous to children and others who suck them), attempts have been made to replace the yellow by the non-poisonous red phosphorus. It was found best to make the head of the match of a mixture of antimony sulphide and oxidising agents (potassium chlorate, potassium bichromate and red lead), and put the red phosphorus with antimony sulphide and gritty material (powdered glass, etc.) on the rubber, or striking surface. Such matches are called safety matches and are supposed to light only on the prepared surface on the box; but they may generally, with difficulty, be ignited by drawing them rapidly across a piece of glass or smooth paper. Many countries have forbidden the use of yellow phosphorus altogether for match-manufacturing purposes; and, in order to produce a match that will light on any dry surface—though not as easily as the old phosphorus match—phosphorus sesquisulphide, P_4S_3, is now used. It is said to be harmless to the workers in the match factories and non-poisonous. To prevent the smouldering of the burnt match after it is blown out, the splints are sometimes soaked in dilute solutions of certain substances, such as magnesium sulphate, and dried before the heads are put on; this is an exceedingly important precaution and should be insisted on by law, as numberless fires are caused by matches that are supposed to be out but which still carry a spark when thrown away.

Compounds of phosphorus.—Phosphorus is a member of the nitrogen family and this fact should be kept in mind, especially in studying its compounds. Although these are very numerous, but few of them need concern us here.

Phosphine, PH_3, gaseous phosphuretted hydrogen, is analogous to ammonia, NH_3.

It may be prepared by heating yellow phosphorus with a strong solution of potassium hydroxide. The gas obtained in this way is spontaneously inflammable on account of the presence in it of small quantities of another compound of phosphorus and hydrogen. Phosphine has a very unpleasant odor, said to resemble that of rotten fish. Although it does not dissolve in water as ammonia does, it will combine with acids to form salts, *e.g.*, PH_4Cl, similar to the ammonium salts. On this account PH[illegible] is called phosphonium.

Phosphorus pentoxide, P_2O_5.—Phosphorus does not form as many oxides as nitrogen—two are well known and some chemists claim to have prepared a third. Only one of them really concerns us here.

Phosphorus trioxide, P_2O_3, or phosphorous anhydride, and its derivative phosphorous acid, H_3PO_3, need be mentioned only on account of the spelling and pronunciation. The noun, phos´-phorus, does not end in -ous, but the adjective, phos-phor´-ous, does end in -ous and is accented on the second syllable.

Phosphorus pentoxide is produced when phosphorus burns in air or oxygen. It is a white, voluminous solid, and its most important property is its intense affinity for water, with which it combines to form H_3PO_4, phosphoric acid. It is the most powerful desiccating (drying) agent we have.

Phosphoric acid, H_3PO_4.—There are several acids of phosphorus, but only one of them will be considered here. Orthophosphoric, or ordinary, phosphoric acid occurs in nature in the form of several of its salts, the most important one being $Ca_3(PO_4)_2$. The acid may be prepared by bringing together phosphorus pentoxide and water, as has already been said, but it is generally prepared by treating phosphorite with sulphuric acid :

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

The $CaSO_4$ is insoluble and may be filtered off. Phosphoric acid is a tribasic acid and can therefore produce a variety of salts :

NaH_2PO_4 . . .	Sodium dihydrogen phosphate	(acid salt)
Na_2HPO_4 . . .	Disodium hydrogen phosphate	(acid salt)
Na_3PO_4 . . .	Normal sodium phosphate	(normal salt)

The second is the compound sold under the name of sodium phosphate.

These salts are sometimes called primary, secondary and tertiary sodium phosphate, respectively.

It is not necessary that the same base should replace the different hydrogen atoms in a polybasic acid; this, $Na(NH_4)HPO_4$ is a well known compound, called microcosmic salt, prepared from urine.

If we consider a double molecule of phosphoric acid, $H_2H_2H_2(PO_4)_2$, and imagine the pairs of hydrogen atoms replaced successively by calcium atoms (diads) we get

$$CaH_4(PO_4)_2$$
$$Ca_2H_2(PO_4)_2$$
$$Ca_3(PO_4)_2$$

The last is the insoluble calcium phosphate found in nature and the first is the principal constituent of "superphosphate," an artificially prepared fertiliser. It is an acid salt, soluble in water.

Fertilisers.—In the natural course of events, plants die where they grew and return to the soil all they took from it plus what they got from the air. Under cultivation, however, crops are removed from the soil and the latter is thereby continually impoverished of certain of its valuable constituents. Some of these constituents of plant food exist only in small proportions in most soils and, unless special precautions are taken, their quantities eventually become so exceedingly small that satisfactory crops can no longer be grown. This is particularly the case with the compounds of nitrogen, phosphorus and potash. As has already been pointed out, nitrogen compounds are replaced by adding ammonium salts, or nitrates. The phosphorus compounds are replaced by adding phosphates. Generally speaking, these must be soluble. $Ca_3(PO_4)_2$ is insoluble, but in years it is slowly converted into soluble compounds in the soil (value of bonemeal); but if we do not want to wait for years, a soluble compound is manufactured and employed, *i.e.*, $CaH_4(PO_4)_2$, "superphosphate," or primary calcium phosphate. We shall see later how potash is replaced. Barnyard manure is perhaps the best of all fertilisers, as it contains practically all the soil constituents necessary for plant growth, including compounds of N, P and K. It cannot, however, be obtained in sufficient quantity to meet modern demands, and hence artificial fertilisers must be employed more and more.

Arsenic.—This element occurs in nature in the native state and also in combination with other elements such as sulphur and the metals.

Realgar, AsS_2, orpiment, As_2S_3, arsenopyrite, FeAsS, are its most important ores.

It is a steel gray solid with a metallic lustre. It is quite brittle and when heated volatilises easily; if air is present, it oxidises, forming As_2O_3, arsenious oxide.

Arsine, AsH_3, corresponding to ammonia and phosphine, is a gas with a peculiar odor and is extremely poisonous.

Arsenious oxide, As_2O_3, occurs as a mineral and is also prepared artificially. It is known as white arsenic (or often, just arsenic) and is very poisonous, being used for killing rats and other vermin and also in minute doses in medicine.

Arsenic compounds are used in the manufacture of certain pigments: Paris green is a compound of copper, arsenic and oxygen, and it is used not only as a pigment but also as an insecticide. All these arsenical pigments are poisonous. Free arsenic is used in small quantities with lead in the making of shot.

Antimony.—This occurs in nature chiefly as stibnite, Sb_2S_3. Its Latin name is *stibium*, from which its symbol is derived. It is still more metallic than arsenic, though brittle and very hard. It expands on solidifying and hence is used in making certain alloys where very sharp castings are required: type-metal is antimony, tin and lead.

Stibine, SbH_3, resembles arsine very closely.

Arsenic and antimony are just on the dividing line between metals and non-metals; free antimony is metallic in almost all its properties, but in its compounds it resembles phosphorus in many ways.

Bismuth.—This is a metal in almost all its properties, but belongs to the nitrogen family; and, as there is very little to be said about it, we may consider it here.

It is somewhat rare and is a heavy, crystalline, brittle metal with a very low melting point, 270°. Many of its alloys melt at much lower temperatures, and, on this account, bismuth is of great value in preparing easily fusible alloys; thus, Wood's metal, which consists of bismuth, lead, tin and cadmium, melts at 60.5°. It is employed for making fusible plugs for automatic sprinkler heads, fusible links for fire doors, etc.

QUESTIONS

1. What is the meaning of the word phosphorus? Has it always been used to designate only the substance we know by that name to-day?

2. Why is there a movement towards making it illegal to use "white" phosphorus in the manufacture of matches?

3. Calculate the percentage composition of phosphoric acid and of normal calcium phosphate. Which is richer in phosphorus?

4. In what ways are nitrogen and phosphorus similar?

5. Some years ago the farmers in a certain part of Canada used to clean up their farm-yards in the winter and dump all the manure on the ice of a near-by river. Criticise this practice, giving reasons.

6. What are the similarities and the differences between ordinary and safety matches?

7. Why is bone-meal valuable as a fertiliser? Why is "superphosphate" more valuable?

8. What is the difference between phosphorous and phosphorus?

9. In lighting a match, how is the phosphorus raised to its temperature of ignition? What is the object of the oxidising agent in the head of the match?

CHAPTER XIV

CARBON. OXIDES OF CARBON. CARBON DISULPHIDE. CARBIDES

In many ways, carbon is the most remarkable of all the chemical elements and it is certainly one of the most useful. As we shall see later on, it forms our principal fuels, producing heat for warming us in winter and for cooking our food, and energy for running our locomotives, steamships and other machinery. Furthermore, by its means, most of the useful metals are produced, as are also glass, china, bricks, lime, cement and a host of other commodities absolutely essential to civilised life. Moreover, the bodies of plants and animals, being largely made up of carbon compounds, their food must contain materials to produce these; and our clothing is very similar chemically.

This element and its compounds, as we should expect from what has been said above, occur in enormous quantities in nature. Coal, which is an impure form of carbon and which is found in a great many parts of the world, is at present being mined at the rate of something like 900 million tons per annum, and at this rate the deposits now known are expected to last for from two to three hundred years—(F. Fischer). Graphite and diamond, which are pure forms of carbon, also occur in many localities. Enormous quantities of carbon, far exceeding that in coal, occur in combination in such rocks as limestone, magnesite, etc., forming huge mountain ranges and underlying vast continental areas. Petroleum is made up of carbon compounds, as are also a large part of the bodies of plants and animals. (Pettenkofer calculates that the body of a man weighing 70 kilos contains 12 kilos of carbon.)

Carbon is an allotropic element ; two crystalline forms are known, diamond and graphite, and there are several amorphous varieties.

Diamond.—Diamonds have been known from very early times and, on account of their extreme hardness and brilliancy, have always attracted more or less attention. The great mathematician, physicist and philosopher, Sir Isaac Newton, conjectured that diamond was related to oils (compounds of carbon) on account of its optical properties ; but it was left for Lavoisier and others working with him to show that, when highly heated in air or oxygen, diamonds burned to CO_2 and must therefore be carbon.

Diamonds are found principally in South Africa, Brazil and the East Indies. Minute ones have also been discovered in meteorites.

Several diamonds have been discovered in the United States, south of the Great Lakes, among rocky material that is known to have been transported from Canada—probably north of Lake Huron—by the huge continental ice sheet during the glacial period ; it is highly probable, therefore, that diamonds will some day be discovered in our own country.

As they occur in nature, diamonds are usually covered with a rough coating which impairs their brilliancy and which is removed during the process of cutting. (It should be remembered that the shapes of cut diamonds are purely artificial and have nothing to do with the natural crystalline form.)

The diamond crystallises in the regular system and is found colorless and transparent, and also of various shades of blue, yellow, brown, etc. Black and opaque diamonds are also found and are known as carbonado or bort. The diamond is the hardest substance known and is quite brittle. It has a specific gravity of 3.5.

The finest diamonds are cut and used as gems (the largest ever found, the "Cullinan," weighed 621 gr. uncut, about 1⅓ pounds avoirdupois); and the poorer ones, including bort and the chips of finer ones, are used for glass-cutting, in drills and in the powdered form for cutting (*i.e.*, grinding) and polishing high-grade diamonds and other very hard substances, such as rubies, etc.

Diamond, when highly heated in air or oxygen, produces CO_2 and nothing else, and is therefore pure carbon. It is attacked by almost no chemicals, but will dissolve in molten iron.

Diamonds have been prepared artificially by Moissan by suddenly cooling intensely hot molten iron saturated with carbon. The diamonds obtained in this way had all the characteristics of the natural ones but were very small, the largest being 0.5 mm. in diameter.

Graphite is found in large quantities in many places, particularly in Siberia, Ceylon, the United States and Canada. It is also prepared artificially. It has a greyish-black color and a metallic lustre, a little like lead, whence its older name of black-lead or plumbago (Latin, *plumbum*, lead). It crystallises in hexagonal plates and is very soft, for a mineral, leaving a mark when drawn across paper; on this account it was called graphite (Greek, *graphein*, to write) and is used in the manufacture of so-called lead pencils. It is also used as a stove-polish and a lubricant. Its density is about 2.3 and, like diamond, when highly heated in air or oxygen, produces CO_2 and nothing else. It is unaltered by most chemical reagents, though not as resistant as diamond, and is soluble in molten iron.

Amorphous Carbon.—Various forms of uncrystallised, or amorphous, carbon are known, both natural and artificial, the principal ones being charcoal, coke, lamp-black and coal. None of these are pure carbon and some of them contain high percentages of intermixed impurities.

Charcoal is prepared by heating wood in iron retorts out of contact with the air, or by burning it in a very limited supply of air. In the latter process, wood is arranged in a low somewhat loose pile and this is covered over with sods and earth to exclude the air, a few openings being left round the bottom. Sometimes the pile is more or less completely enclosed in masonry, forming what is known as a charcoal kiln. The pile of wood is lighted at the bottom and a smouldering fire maintained for some days, great care being taken to fill up any cracks which may form in the covering. After a time all openings are completely closed and then the burning stops for lack of air, and the heap is allowed to cool.

Charcoal is a black, softish solid, very porous; when heated in air it takes fire easily. It was formerly used a great deal as a fuel in chemical and metallurgical operations, as it produces a very hot, clean fire; but, on account of the growing scarcity of wood, it is rarely used in this way at the present time. Like other forms of carbon, it is very resistant to the attacks of various chemicals (hence the occasional practice of charring those portions of fence-posts which are to be buried in the ground).

Coke.—This is produced by heating soft coal in retorts (in the making of coal gas) or coke ovens, out of contact with the air. It is very much harder than charcoal and is used as a fuel, particularly in metallurgical operations. It contains all the ash of the original coal.

Lamp-black is a form of (impure) carbon deposited from the smoky flames of burning coal, oil, etc. It is used in the manufacture of printers' ink and paints.

Bone-black, or animal charcoal, is obtained by heating bones out of contact with the air. It contains a very high proportion of mineral matter (phosphate of lime) and is much used as a filtering agent for extracting the coloring matter from solutions of sugar in the process of refining.

Coal has been formed from vegetable matter (compounds mainly of carbon, hydrogen and oxygen) which was deposited in enormous quantities in swamps as peat, and afterwards underwent a very slow process of decay beneath layers of rock formed from mud which was deposited over the peat. According to the amount of change that has taken place, we have peat, brown coal (lignite), soft coal (bituminous coal) or hard coal (anthracite), this last being almost pure carbon mixed with mineral matter (ash). All these substances are used as fuels, peat being the least valuable on account of the large proportion of water which it contains and the difficulty of drying it out. They all produce CO_2 on burning (and also H_2O from their content of hydrogen).

The various forms of carbon described above differ in some ways and are alike in others. They differ in appearance, in hardness, in density, etc., but they are all solids, odorless, tasteless, insoluble in water and unaltered by most chemical reagents. When highly heated in air or oxygen they all burn, producing CO_2 (if sufficient oxygen be present), thus showing that they are all forms, more or less pure, of [illegible] the same element, carbon. On account of its great affinity for oxygen at high temperatures, carbon is a very powerful reducing agent and, as many metals occur [illegible] as oxides, carbon (charcoal, coke, coal) [illegible] extent in metallurgy for reducing th[illegible] metallic state.

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

Carbon combines with oxygen in two [illegible] two very different compounds, carbon monoxide [illegible] dioxide, whose compositions are represented by the [illegible] CO and CO_2. For certain reasons, it [illegible] well to consider carbon dioxide first.

Carbon dioxide, CO_2 (carbonic acid gas). This compound is particularly interesting [illegible] one of [illegible] gases to be recognised as differing from common air (van Helmont, 1640), [illegible] carefully studied [illegible] the Scotch chemist, Joseph [illegible] who called it fixed air, but did not discover its [illegible]on. Lavoisier showed that it was composed of [illegible] and oxygen.

[illegible] already seen, it forms a small but very important [illegible] atmosphere; it issues from cracks in the earth [illegible]es; some mineral spring waters contain [illegible]tities that they effervesce when [illegible] are [illegible] (Apollinaris, Vic[illegible] Seltzer), and almost [illegible]ntain a little of it [illegible] solution; and it is [illegible] processes of combustion, fermentation, [illegible]on. [illegible]rther, it occurs in combination in [illegible]erals, such as [illegible]estone.

[illegible] dioxide is sometimes found in considerable quantity in unused [illegible] and in wells. Should it be necessary to enter such places, it is well first [illegible] the air by lowering a lighted candle. [illegible] the candle will burn, the [illegible] of carbon dioxide is not dangerous.

Carbon dioxide is produced wh[illegible]rbon (or any of its compounds) burns in an excess of [illegible]ygen. It may be [illegible]d by treating almost any [illegible] such as sodium [illegible]ate (washing soda) or calcium [illegible]ate (limestone, marble) with an acid; in the laborator[illegible] usually prepared [illegible] the action of hydrochloric acid on marble. An ordinary metathetical reaction takes place:

$$CaCO_3 + 2HCl = CaCl_2 + H_2CO_3$$

but the H_2CO_3, carbonic acid, is very unstable and most of it decomposes:

$$H_2CO_3 = H_2O + CO_2$$

EXPERIMENT.—Fit up an apparatus as represented in the figure, and put some marble chips into the flask. Run dilute hydrochloric acid in through the thistle-tube, and collect a cylinder of the gas produced, by downward displacement. Is the gas heavier or lighter than air? Why do you think so? Test the gas with a burning taper. Does it burn? Does it support combustion? Collect a second cylinder of the gas and pour it over the flame of a burning candle (the wick should be very short and the flame very small unless a very large quantity of the gas is used). What happens? What does it show with regard to some physical and some chemical properties of the gas? Collect a third cylinder of the gas and introduce into it a burning piece of magnesium. What happens? Observe the oxide of magnesium formed. How do we already know the composition of this substance? What does its formation here prove concerning the gas? Dissolve the oxide by means of some dilute hydrochloric acid. Notice the black carbon which is left. Where did it come from? What does it prove with regard to the gas? What does this experiment prove as to the qualitative composition of the gas? Pass a little of the gas into lime-water. Blow through a tube into another portion of lime-water. What happens in each case? How do you explain it? (See below.)

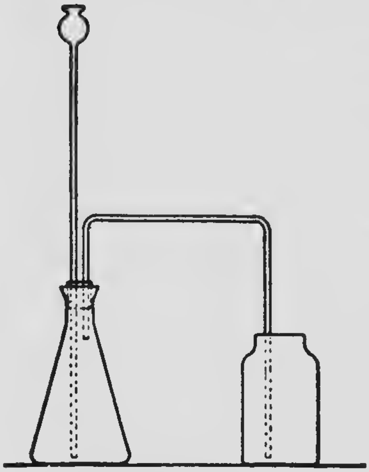


FIG. 20.

Carbon dioxide is a gas, colorless, odorless and heavier than air, the G.M.V. weighing 44 gr.

CO_2 may be liquefied by pressure at ordinary temperatures, about 800 lbs. to the square inch being required; the liquid is sold in steel cylinders, which must of course be able to withstand this pressure. ("Sparklet" bulbs contain liquid CO_2.) If this liquid be allowed to run out into some sort of loose bag, the intense cold caused by the rapid evaporation of some of the liquid causes the rest to solidify to a white, snow-like mass, the temperature of which is about -65° and can be reduced to about -110° under the receiver of a good air pump.

For commercial purposes, carbon dioxide is often prepared by heating magnesite, a commonly occurring mineral,

$$MgCO_3 = MgO + CO_2$$

Under ordinary conditions, water dissolves its own volume of CO_2, and the solubility increases directly with the pressure (general law for all gases); water saturated with CO_2 under a pressure of three or four atmospheres is what is known as soda-water (the CO_2 for this purpose having been formerly prepared from sodium carbonate, or soda, hence the name).

From the fact that carbon dioxide is produced by burning carbon, we should expect to find it incombustible—which it is. Further, it will not support ordinary combustion. For this reason it is often made use of for putting out fires—many fire-extinguishers contain a solution of a carbonate, such as baking soda, and a bottle of sulphuric acid; when the extinguisher is set in action, *e.g.*, by turning it upside down, the acid acts on the carbonate and an effervescent solution of CO_2 is produced which is squirted on to the fire, putting it out. A few substances, such as burning magnesium, are capable of robbing CO_2 of its oxygen and will, therefore, burn in it.

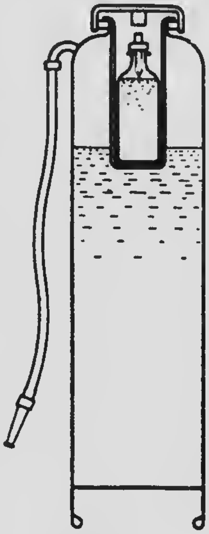


FIG. 21.

Carbonic Acid, H_2CO_3.—Carbon dioxide dissolves in water, as has already been stated, combining with it to form carbonic acid. Hence, CO_2 is an acid anhydride, carbonic anhydride. Carbonic acid is very unstable, breaking down easily into CO_2 and H_2O. It is a dibasic acid and many of its salts, the carbonates, are very important, as we shall see later.

Carbon dioxide and carbonic acid are recognised by their power of turning lime-water milky. The reactions involved are the following: the CO_2 reacts with H_2O to form carbonic acid,

$$CO_2 + H_2O = H_2CO_3,$$

and then this acid reacts with the slaked lime in solution, a base, to produce water and calcium carbonate:

$$H_2CO_3 + Ca(OH)_2 = 2H_2O + CaCO_3,$$

and, as the $CaCO_3$ is insoluble in water, it is precipitated (separates out as a finely divided solid), imparting a milky appearance to the liquid. The same thing happens when air from the lungs is passed into lime water.

When carbon dioxide and water meet in the green leaves of plants, certain very complex reactions take place, under the influence of sunlight, whereby starch, $C_6H_{10}O_5$, is produced and oxygen liberated. These reactions may be summarised as follows:

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

A large quantity of energy, furnished by the sunlight, is used up in this reaction, and exactly the same quantity of energy would be re-obtained, as heat, if the starch were burned in oxygen, *i.e.*, the above reaction reversed. This, then, shows that solar energy is the source of the heat we get from fuel, it having been stored up in the vegetable matter from which the fuel is produced.

Carbon monoxide, CO.—This compound does not occur in nature, but it is formed when carbon (or a substance containing it) is burned in a limited supply of air or oxygen:

$$C + O = CO$$

It is also produced when CO_2 is passed over highly-heated carbon:

$$CO_2 + C = 2CO$$

In this way it is formed in ordinary stove or grate fires. The oxygen (or air) entering at the bottom combines with carbon of the fuel to form CO_2, the air being in excess, and this CO_2, rising through further layers of very hot fuel, is reduced to CO, carbon being in excess, and the CO burns at the top of the coal, provided that it is hot enough and that there is a sufficient supply of oxygen (fresh air). Should it escape unburned into the air of the room, it is exceedingly dangerous.

Carbon monoxide is formed along with hydrogen when steam is passed over very highly-heated carbon

$$C + H_2O = CO + 2H$$

and the gas thus obtained is known as "water gas." It is a valuable fuel, but, although the flame is very hot, it is pale and gives almost no light. As water gas—on account of its content of CO—is very poisonous, and has but little odor, its use is attended with considerable danger, and is not permitted in certain countries.

Carbon monoxide is a gas, colorless, tasteless and with a slight peculiar odor. The G.M.V. weighs 28 gr. (same as nitrogen). It is insoluble in water and will not support combustion, but it burns with a pale blue flame, forming CO_2, and is an excellent reducing agent. Thus, when passed over heated copper oxide, metallic copper is obtained :

$$CuO + CO = CO_2 + Cu$$

Carbon monoxide is extremely poisonous, even small quantities proving fatal when inhaled.

Carbon disulphide, CS_2.—As has already been seen, oxygen and sulphur are similar in many ways ; and just as oxygen at a high temperature combines with carbon to form carbon dioxide, so sulphur combines with carbon to form carbon disulphide. This latter compound is a heavy, colorless liquid, generally possessing a disgusting smell, though the perfectly pure substance is said to have a pleasant aromatic odor. It boils at a low temperature and its vapor is very inflammable. It is used for dissolving rubber, sulphur, etc.

Just as there is the acid, H_2CO_3, corresponding to CO_2, so there is an acid, H_2CS_3, corresponding to CS_2, another resemblance between oxygen and sulphur.

Hydrocyanic acid, HCN, prussic acid. This is a weak, very volatile acid with an odor resembling bitter almonds. It is soluble in water and is extremely poisonous, one or two drops of the solution sometimes proving fatal. Its salts are called cyanides.

Carbides.—Many metals can be made to combine with carbon, the products being called carbides. The most important of these is calcium carbide, CaC_2, which, when brought into contact with water, gives acetylene, C_2H_2 :

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2$$

QUESTIONS

1. How do we know that the different allotropic forms of carbon are really forms of one and the same element?

2. Why is carbon called a reducing agent?

3. Can you imagine any cause for the difference between diamond and graphite? (*Cf.* oxygen and ozone.)

4. Why does soda-water effervesce when the bottle is uncorked?

5. What is the action on a fire of the liquid from a fire-extinguisher?

6. How may (*a*) CO and CO_2 and (*b*) CO and H_2 be distinguished in the laboratory?

7. It is sometimes said that certain gases may be recognised by their poisonous properties. Would you care to recognise gases yourself by this test? Do you, then, consider it a good test to quote?

8. Two persons are found early in the morning, after a very cold night, asphyxiated in a small house: What cause would you suspect?

9. How does the use of stove-polish prevent rusting?

10. How do we know that coal is not pure carbon?

11. A certain volume of carbon monoxide is burned. What volume of carbon dioxide will be produced?

12. How many molecules of carbon dioxide does one molecule of carbon monoxide produce when it burns? How many molecules of oxygen does it use up in so doing?

13. A mixture of equal volumes of carbon monoxide and oxygen are exploded in a eudiometer. What volume of gas will be left in the tube after the experiment, and what will be its composition?

14. What elements so far studied exhibit allotropy?

15. What chemical reactions go on in an ordinary hard-coal or charcoal fire?

16. Why is a pan of smouldering charcoal dangerous in a room?

17. What gases are found in solution in most natural waters? Mention another gas found in solution in some springs.

18. How can you account for the very slight sour taste which soda-water has?

19. Why do you think meat and vegetables turn black when "burned"?

20. How might it be shown that carbon dioxide is contained in the air breathed out from the lungs?

21. What is the objection to the use of "water-gas" as a domestic fuel?

CHAPTER XV

OTHER COMPOUNDS OF CARBON. ORGANIC CHEMISTRY

About two hundred and fifty years ago, chemical compounds were divided into two large classes: organic and inorganic. The former were those found in organisms, *i.e.*, in plants and animals; and the latter, those found in the mineral kingdom. It was long believed that, while inorganic compounds could be prepared in the laboratory, organic compounds could not: that they were produced only in living plants or animals under the influence of a peculiar force, the life force, *vis vitalis*, and could not be made artificially from dead matter. However, in 1828 Wöhler, a German chemist, prepared a typical compound, *urea*, in the laboratory, from an ordinary inorganic compound. Since that time, an enormous number of other so-called organic compounds have been built up from their elements (synthesised) in the laboratory—including for instance, grape-sugar (glucose)—and this, of course, has made it necessary to give up the old idea connected with the life force. However, on account of the very great variety of these carbon compounds—about one hundred thousand of them being well known—and their more or less intimate relations, one to another, they are classed together for convenience of study, and the branch of chemistry dealing with them is still called organic chemistry. Nevertheless, it must be carefully kept in mind that the division of compounds into organic and inorganic is not a necessary one, depending on fundamental differences, but only a useful one designed for certain practical purposes.

As can be easily understood, nothing but the most limited references to a very few of these substances can be made in this place. But, on account of the supreme importance of many of them in everyday life, it would be unwise to overlook them altogether, in spite of the complexity of their thorough treatment. Fortunately their study is much simplified by the possibility of arranging them in a comparatively small number of groups, a condensed classification being here appended.

HYDROCARBONS:
- Paraffins—Methane, Petroleum.
- Acetylene.
  - Illuminating gas. Flame. Davy lamp.
- Derivatives of paraffins:
  - Halogen—Chloroform.
  - Hydroxyl — Methyl alcohol; Distillation of wood. Ethyl alcohol; Fermentation. Glycerine; Nitro-glycerine.
  - Oxides—Ether.
  - Salts—Etherial salts.
  - Acids—Fatty acids. Vinegar. Soap. (Other acids.)
- Aromatic compounds,
  - Benzol.
  - (Phenol, di-hydroxy derivatives, aniline.)

CARBOHYDRATES:
- Glucose.
- Saccharose. Manufacture of sugar.
- Lactose.
- Cellulose—Cotton, linen, wood, paper, gun-cotton, celluloid.
- Starch—Vegetable food.

PROTEÏDS:
- Gluten—Flour, bread - making. Meat.
- Albumen.
- Legumin.
- Caseïn—Milk.

ALKALOIDS.

The proportion of carbon and hydrogen in organic compounds is determined by burning known weights of the compounds in oxygen (combustion) and collecting and weighing the CO_2 and the H_2O produced; the proportions of other elements, if present, are determined by suitable tests; and then the proportion of oxygen, if present, is determined by difference, no really satisfactory method of determining it directly having yet been devised. The formulas are worked out from the analytical results and the molecular weights in the usual way (p. 77).

Hydrocarbons.—A large number of compounds of carbon and hydrogen are known, and these are called hydrocarbons. (Do not confuse this term with carbohydrates—these latter contain oxygen, as is indicated by the termination *-ate.*)

Paraffins.—*Methane*, CH_4.—This is the only hydrocarbon containing one atom of carbon in the molecule. It is the principal constituent of natural gas, and also forms a large proportion of coal gas. Further, it is found, along with other gases, in the bubbles rising from swamps, and hence it is often called marsh-gas ; it also issues from the masses of coal in coal mines, where it is known as fire-damp.

The natural gas from a gas-well at Baku, near the Caspian Sea, is burning, ignited possibly by lightning, and is known as the "Holy Fire of Baku," being held as very sacred by the fire-worshippers.

Methane is easily prepared in the laboratory and is a gas, colorless, odorless and tasteless, and burns with a pale blue flame. If plenty of air or oxygen be present, the products of the combustion are H_2O and CO_2, but if insufficient oxygen be present, CO is formed as well.

Any combustible substance (solid, liquid or gas) if intimately mixed with air or oxygen (the solid must be very finely pulverised and the liquid vaporised or "atomised"), gives a mixture which will explode on ignition: the heat produced causes such an expansion of the gases resulting from the combustion that they tend to break down all barriers—and of course there is grave danger to human life in such a happening. In the case of a fire-damp or coal-dust explosion in a mine, there is also further danger : the oxygen of the air is used up, producing CO_2 which will not support respiration and therefore induces suffocation, or CO, which is actively poisonous. The CO_2 produced in such an explosion is called after-damp or choke-damp by the miners.

Marsh gas is the first of a series of hydrocarbons, called paraffins, each member of which differs from the next by CH_2. Such a series is called a homologous series.

PARAFFINS

CH_4	Methane	C_5H_{12}	Pentane
C_2H_6	Ethane	C_6H_{14}	Hexane
C_3H_8	Propane	C_7H_{16}	Heptane
C_4H_{10}	Butane	C_8H_{18}	Octane

Most of the members of this series are known up to about $C_{60}H_{122}$; the lower ones are gases, followed by liquids with rising boiling points, and these by solids with rising melting points.

The general formula of this series is C_nH_{2n+2}. Another series, the ethylene series, is C_nH_{2n}; the acetylene, C_nH_{2n-2}; and there are other series of hydrocarbons, the most important of these being the aromatic or benzene series, C_nH_{2n-6}. The hydrocarbons form very striking examples of the law of multiple proportions, though the "small whole numbers" here may run up to 100 or more.

Petroleum is mainly a solution of hydrocarbons of this series, paraffins, the gaseous and solid ones being dissolved in the liquid ones. On careful heating, the gases come off first, then the low-boiling liquids and then the high-boiling ones. By collecting the different portions separately (and redistilling), various products are obtained which are not definite chemical compounds, but solutions of compounds having boiling points lying very close to one another. The products are often freed from impurities by washing with sulphuric acid, with an alkali and with water.

Some of the commercial products, with their *approximate* compositions and boiling points, are as follows:

Cymogene	mainly	C_4H_{10}	1°
Rhigolene	"	C_5H_{12}	38°
Gasoline	"	C_6H_{14}	71°
Naphtha	"	C_7H_{16}	98°
Benzine	"	C_8H_{18}	124°
Kerosene	"	$C_{12}H_{26}$ to $C_{16}H_{34}$	214°
Lubricating oils			
Vaseline	"	$C_{22}H_{46}$ to $C_{23}H_{48}$	
Paraffin wax	"	$C_{24}H_{50}$ to $C_{28}H_{58}$	

Of course these products vary a great deal according to the way in which the fractional distillation is carried out, hence it is often necessary to have them tested by trained chemists (*e.g.*, kerosene, for its flashing-point, *i.e.*, the temperature at which it gives off sufficient vapor to take fire).

Acetylene, C_2H_2, is a hydrocarbon belonging to another series. It is prepared by bringing calcium carbide and water together:

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2$$

It is a gas with a disagreeable smell (most of the odor of commercial acetylene, however, is due to impurities, largely PH_3) and burns ordinarily with a smoky flame. If a special form of burner be used, so that the flame is very thin and therefore gets a large proportion of oxygen, no smoke is given off and a very brilliant light is produced. This is used for illuminating purposes where coal gas or electric light cannot be obtained. It is very dangerous to store acetylene alone under pressure, as it is liable to decompose spontaneously with explosive violence. It may, however, be stored in solution (in acetone or some other solvent) under pressure and then there is no danger of explosion. In this form it is used in railway cars, in automobiles, etc.

Methane, acetylene and some other hydrocarbons are more or less decomposed with separation of free carbon when heated out of contact with the air. This has an important bearing on the luminosity of flames, as we shall see presently.

Coal gas is prepared by heating soft coal in retorts, cooling the gases given off to separate the tar, passing them through water to extract the ammonia and then freeing them from disagreeable sulphur compounds. Coke is left behind in the retorts. The gas thus obtained contains almost 50% of hydrogen, about 35% of methane, about 5% of compounds that burn with luminous flames (acetylene, ethylene, benzene, etc.), and other constituents.

Water gas, which burns with a pale blue flame, is often "enriched" by adding to it gases produced by dropping petroleum on to white hot bricks, these gases burning with luminous flames; further, the enriching imparts a strong disagreeable odor to the gas which renders its use much less dangerous (on account of its poisonous nature) than if it were odorless.

Oil gas (Pintsch gas, Blaugas) is prepared by dropping petroleum into a white hot tube (which decomposes, "cracks" it) and collecting the resulting gases.

Flame.—The term combustion has already been defined as signifying an act of chemical combination accompanied by the production of heat and, generally, light. If one of the substances undergoing combustion is a solid, and the product is a solid at the temperature of the reaction, no flame will be produced. This was the case with the burning iron, as described on p. 31. If, however, the substances concerned are gases (or vapors) at the temperature of the reaction, then a flame is produced. We have therefore the following definition: *A flame is a current of burning gas.* This is obvious enough in the case of burning hydrogen, coal gas, acetylene; but how is it with kerosene, candles, wood, etc.? In the case of a kerosene lamp the oil is drawn up, by the capillary action of the wick, into the flame and there it is boiled and converted into vapor by the heat, thus supplying the flame with a current of inflammable gas. In the case of a burning candle, the heat of the flame melts the grease at the top of the candle, the wick thus rising from a saucer-shaped depression filled with oil, and this oil is drawn up by the wick into the flame and there vaporised exactly as in the case of an oil lamp, as just described. A lamp or candle, then, is a miniature gas factory. In the case of wood, the heat of the flame decomposes the wood—subjects it to destructive distillation—some of the products being inflammable gases. If a candle flame be examined, it will be seen to consist of at least three conical portions, one inside the other (Fig. 22), the innermost appearing dark in color, the next one bright and yellowish, and the inner one pale blue. The inner one, which is called the *area of non-combustion*, consists of the current of inflammable gas already mentioned, rising from the wick. This may be shown by carefully

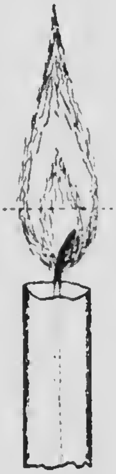


FIG. 22.

inserting the end of a thin glass tube, about 8 mm. in diameter and 3 cm. long into the middle of this cone just above the wick, and holding the tube nearly vertical. In a minute or two vapors will be seen rising from the top of the tube and may be ignited. The same thing may be shown by blowing out the flame of a candle having a long wick, when a little stream of whitish vapor will be seen rising from the hot wick for a few seconds; by holding a lighted match in this about three-quarters of an inch from the wick, a tiny flame will be seen to run down it to the wick. (The reason why a *cold* candle wick does not take fire instantly on touching it with a match, as the hot wick just mentioned would do, or as a current of gas will, is that sufficient time must be allowed for the heat from the match (1) to melt the grease in the wick and (2) to volatilise some of the oil thus produced, as well as (3) to raise the vapor to its temperature of ignition.) That no combustion takes place in the inner cone and that it is cool compared with the next one can be shown by quickly moving a piece of paper horizontally into the flame, as indicated by the dotted line in the figure, holding it there a second or two and rapidly withdrawing it. The paper will be singed in a ring and not singed in the centre. In the second, or luminous area, burning is going on, some air having become mixed with the inflammable gas, though the latter is in excess, and the temperature is quite high. Here some of the hydrocarbons of the gas are decomposed by the heat, a little free carbon in the form of lamp-black being liberated, some such reaction as the following taking place:

$$2C_2H_2 = CH_4 + 3C$$

This carbon is in the solid state and is intensely hot and glowing; *the cause of the luminosity of all ordinary flames is the presence in them of incandescent* **solid** *matter.* The presence of the free carbon (lamp-black) in this part of the flame may be proved by holding in it some cold solid object such as a porcelain dish, when a black deposit will be obtained. In this part of the flame, as has already been said, combustion is going on, the hydrogen and carbon being oxidised, at least in part; hence, this is called the *area of partial combustion.* Some of the combustion, however, takes place beyond where any solid carbon exists, *i.e.*, after all carbon has been converted into CO; and the burning of this (with some hydrogen, too) produces the outside, pale blue cone, the *area of complete combustion* (sometimes called the mantle). The products of complete combustion are CO_2 and H_2O. If insufficient oxygen be present, as in the case of a kerosene lamp turned too high, or a candle with a wick that has become too long, only partial combustion takes place, the flame "smoking," *i.e.*, some of the free carbon escaping along with some CO and other products.

If the inflammable gas in an ordinary flame be diluted with sufficient air before it is ignited, the separation of free carbon is prevented and the result is what is called a non-luminous flame, the areas of partial and of complete combustion becoming one. This is the principle of the bunsen burner (invented by the German chemist Bunsen), the inflammable gas being practically never in excess of the air—air being supplied from within as well as from outside the flame. Modified forms of this burner are used in connection with Auer light mantles and also in gas stoves, blue-flame oil stoves, etc. The bunsen burner is constructed as in the figure, the gas issuing from the jet A, drawing some air through the holes B, B, and the mixture

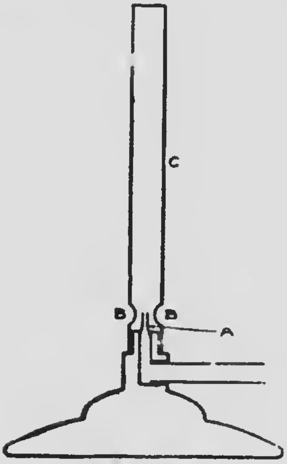


Fig. 23.

rising through the tube C to burn at the top where more air is obtainable. If too much air be admitted through the holes at the bottom, the flame becomes noisy, owing to a succession of minute explosions, and may travel back down the tube C, the gas then burning (incompletely) at the jet A. This is dangerous in two ways: the lamp gets so hot that some of its joints may come apart, or the rubber tube by which it is connected to the gas supply may be melted off; and the combustion will be incomplete, certain very objectionable products, such as C_2H_2 and CO being given off into the air.

In experimenting with a bunsen burner, it will be observed that the more air admitted at the base, the supply of gas being kept uniform, the smaller is the flame. The small flame is hotter than the large one because the same quantity of gas is being burned in a small space and hence the heat is more concentrated. It must be carefully kept in mind that *the total quantity of heat produced by burning a certain quantity of a given fuel* (solid, liquid or gas) *is always the same,* no matter how the burning is carried on, provided, of course, that combustion is complete, *i.e.*, that all the fuel is really burned. It is [illegible] that the quantity of air necessary for the complete combustion of this fuel is absolutely fixed (law of constant proportions) and, therefore, that the introduction of more air than is necessary for this complete combustion is wasteful, as the extra air just carries away heat without helping to produce any. Hence, advertisements of stoves, etc., that "burn more air than any other" are to be regarded with suspicion.

The free carbon in a kerosene, gas or other flame is an agent for converting some of the heat into light, but it is a rather inefficient agent, there being other substances that will turn a larger proportion of the heat into light. The most efficient material for this purpose yet found is used in making

Auer light mantles (see p. 243). Such a mantle consists of an open-work cone made of a mixture of the oxides of the rare metals thorium and cerium and, when properly suspended in a non-luminous bunsen flame, converts about five times as much heat into light as the carbon would do.

There is one other point in connection with flames that should be noticed, and that is that an inflammable substance, in order to burn, must not only be supplied with sufficient oxygen (air), but must also be at a temperature equal to or above its temperature of ignition. The reason why a candle flame deposits soot on a cold object introduced into it is because the object cools the carbon that touches it below its temperature of ignition and keeps it there; then it cannot burn, no matter how much oxygen may be present. If one end of a piece of copper wire (a good conductor of heat) be held in a flame, the wire extracts heat from the flame and gets hot for some distance from the end, and the flame, as it passes the wire, must be correspondingly cooled. If many wires be introduced into the flame, the gases, as they pass them, may become cooled below their temperature of ignition and then will not burn beyond the wires.

Experiment.—Light a bunsen burner and turn off the supply of air at the base; then holding a piece of fine wire gauze horizontally, bring it down slowly till it is about an inch above the burner. Notice that the flame does not pass through it. To show that the gas is passing through, bring a lighted match above the gauze, when the gas will be ignited. Turn out the burner; then, still holding the gauze about an inch above the opening, turn on the gas and light it above the gauze. The flame does not pass downwards through the gauze. Gauze made of copper wire is best for these experiments, because copper is such a good conductor of heat. Very open gauze made of fine wire, like mosquito netting, will not do, as there is not enough metal in it to carry off the heat quickly enough.

A flame then can pass only with great difficulty through metal gauze. This is the principle of the safety lamp invented by Sir Humphrey Davy (1815). In its original form, this was a small oil lamp having a sort of chimney about 2 inches in diameter and 8 inches high, made of wire gauze. In accordance with the principle just enunciated and illustrated, no flame could pass through the gauze to the air outside even if this latter contained sufficient fire-damp (methane) to be explosive; however, some of this mixture could pass inside the gauze, making its presence known by tiny explosions there, or an alteration in the character of the lamp flame and thus warning the miner of his danger. Since Davy's time the lamp has been much improved, the lower part of the gauze cylinder being replaced by heavy glass, automatic lighters being introduced, etc.

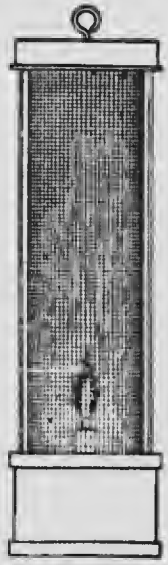


FIG. 24.

Derivatives of Paraffins.—If we imagine one of the hydrogen atoms in the molecule of a hydrocarbon taken away, and its place taken by some other univalent element (such as Cl or Br) or group (such as OH or NO_3), the resulting compound is called a substitution product, or derivative, of the hydrocarbon. We also obtain such products by the replacement of two or more hydrogens, and, according to the nature of the substituting elements, or groups, we obtain different classes of derivatives: halogen derivatives, hydroxyl derivatives, oxides, acids, salts.

Halogen Derivatives of Paraffins.—Starting with methane, CH_4, we can imagine one, two, three, or four hydrogens replaced by a corresponding number of Cl atoms, giving us CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, mono-chlormethane, di-chlormethane, tri-chlormethane, tetra-chlormethane or carbon tetrachloride. All these compounds are known; monochlormethane, or methyl chloride, is used for freezing the flesh in surgical operations; tri-chlormethane is chloroform, a colorless liquid used as an anæsthetic; and carbon tetrachloride is a liquid which will dissolve fats and oils, as gasoline does, but which is non-inflammable. The iodine compound that corresponds to chloroform, *i.e.*, tri-iodomethane, CHI_3, is iodoform, a yellow solid, and is much used as an antiseptic in the dressing of wounds.

Hydroxyl Derivatives.—The hydroxyl derivatives of the paraffins, obtained by replacing one or more H atoms by a corresponding number of hydroxyl groups, are what are known as alcohols; thus, methyl alcohol is CH_3OH (derived from CH_4) and ethyl alcohol is C_2H_5OH (from C_2H_6). (These compounds resemble bases in their action towards acids.)

Methyl alcohol, CH_3OH, wood alcohol, wood spirit, is one of the products of the destructive distillation of wood. When wood is heated in closed retorts and the vapors given off are condensed, a large number of products are obtained, the two most important being methyl alcohol and acetic acid (pyroligneous acid). The various products are separated by suitable processes. Methyl alcohol is a colorless liquid with a characteristic odor; it is lighter than water (Sp. gr. 0.8) and boils at 67°. It mixes in all proportions with water. Like ordinary alcohol, it burns with a flame that is almost colorless and hence is used on the small scale as a fuel (alcohol lamps, etc.). It is also used as a solvent for gums, etc. (shellac). It is poisonous, and the continued breathing of air containing its vapor (as in varnish works) is said to produce blindness.

Formaldehyde, HCHO, is an important compound prepared from methyl alcohol. It is a gas with powerful antiseptic and disinfecting properties. A 40 solution in water is known as formalin.

Ethyl alcohol, C_2H_5OH, common alcohol, spirits of wine.—This compound is produced by the fermentation of glucose, which occurs in fruits, and which is easily produced from ordinary sugar or starch (also from wood). Yeast, which is a microscopic plant, will grow in a solution of glucose (best at 30°), and the glucose is broken down into alcohol and carbon dioxide :

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

If the fermented liquid be heated in a vessel connected with a condenser, alcohol, which boils at 78°, distils over first with a very little water; as the distillation goes on, less and less alcohol and more and more water come over. By catching the distillate in separate portions and redistilling them in the way already described, a further separation of the alcohol and water can be effected, until the alcohol is obtained almost pure (about 98%). The process thus outlined is called fractional distillation and is carried on automatically on the large scale.

EXPERIMENT.—Fit a 500 cc. flask with a tightly fitting cork through which runs a glass tube bent twice at right angles so as to extend almost to the bottom of a small beaker. Measure out 350 cc. of a 20% solution of glucose and place it in the flask. Cut up half a yeast cake, place the pieces in a test-tube and shake with water until they are thoroughly broken up and add the mixture to the solution in the flask. Half fill the beaker with lime-water and, to prevent diffusion into it of CO_2 from the air, cover with a piece of paper pierced with a hole just large enough to admit the passage of the tube from the flask, and pour a little kerosene on to the lime-water and set the apparatus aside for a few days and note what happens. What evidence is there of the evolution of CO_2?

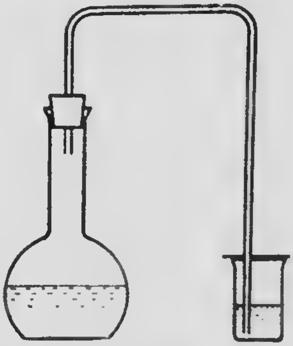


FIG. 25.

Fasten the flask containing the solution on a retort stand and attach it through the rectifier to a condenser (Fig. 26). Then gradually warm the solution until it boils. The vapor evolved at first will consist mainly of alcohol. Why? Will it contain any water? Why? Collect the first drops of the distillate in an evaporating dish and ignite them.

Ethyl alcohol is a colorless liquid with a pleasant odor; it is lighter than water (Sp. gr. 0.78) and boils at 78°. It mixes with water in all proportions and burns with a blue flame; hence, it is used as a source of heat in small stoves, etc. When taken into the system in comparatively small quantities it produces intoxication; in very large quantities it is poisonous. It is a valuable solvent for many substances, the alcoholic solutions being called tinctures.

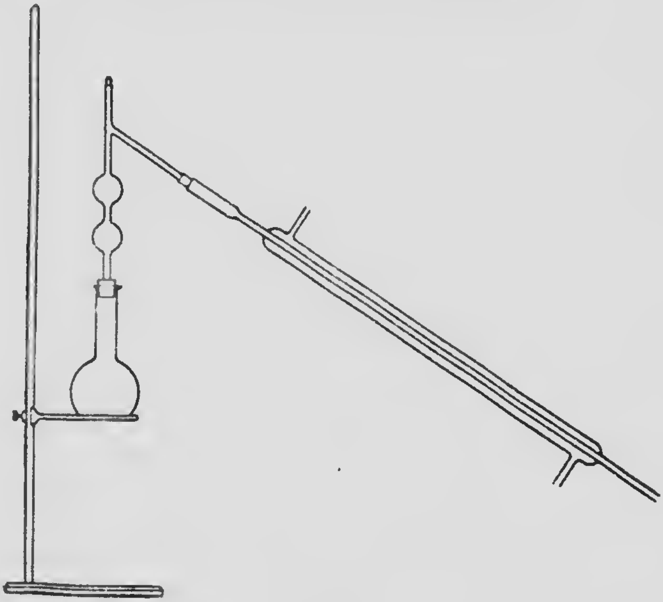


FIG. 26.

Enormous quantities of alcohol are used every year in alcoholic beverages such as beer, wine and whiskey. Beer (porter, stout) is produced by allowing barley to sprout whereby its starch is converted into a compound very like glucose; the sprouting is stopped at the right time by heating and the product is known as malt. This malt is put into water, yeast and hops are added, and, after fermentation has gone on for a certain length of time, the product is strained and put in barrels or bottles. Further fermentation takes place and the CO_2 produced, being unable to escape, dissolves and causes the liquid to effervesce when poured out. Wines are made by fermenting grape juice (cider is similarly made by fermenting apple juice, perry from pears and mead from honey). Whiskey, brandy, gin, rum, etc. (known as spirits), are made by distilling fermented liquids obtained from grains, potatoes, fruits, molasses, etc. (that is, substances that contain glucose). Beer contains 2 – 7% alcohol ; wines, 7 – 20% ; and distilled liquors (spirits) about 50%.

Alcohol is being used more and more as a fuel, and ethyl alcohol is cheaper to produce than methyl.

The production of cheap alcohol for fuel and other industrial purposes is an exceedingly important problem to-day, especially as the price of gasoline is rising so much. Ethyl alcohol can now be produced more cheaply than methyl—probably at about 15-18 cents per gallon (91)—but as the government imposes an excise duty of something like two dollars a gallon, it becomes far too expensive to be used as fuel, except on the very small scale. If, however, it be rendered undrinkable, by the addition of methyl alcohol (forming methylated spirits) or some other disagreeable or poisonous liquid, it is then known technically as denatured alcohol and is exempt from this high tax while still about as valuable as a fuel and for various other industrial purposes. Alcohol for these purposes can be made from rotten potatoes, musty grain and other materials of small value ; and recent experiments in making it from sawdust appear to have been moderately successful. As these processes are studied and developed, the manufacture of alcohol from a very large number of cheap sources will become more and more economical, with the result that a most valuable fuel for internal combustion engines and other purposes will be obtainable at reasonable rates. They have already made great strides in these directions in Germany and some other countries.

Glycerine, $C_3H_5(OH)_3$.—The third member of the paraffin series is propane, C_3H_8. If we imagine three of the hydrogens in this molecule replaced by three hydroxyls, we have glycerine. This compound is prepared in the manufacture of soap (see p. 178) and is a colorless, odorless, syrupy liquid, with a sweet taste. When treated with very strong nitric acid, water and a nitrate called glyceryl trinitrate are formed:

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O$$

This glyceryl trinitrate, or nitro-glycerine, is a colorless, oily liquid, insoluble in water. If quickly heated, or if subjected to shock, it explodes (decomposes) with great violence. Dynamite is produced by absorbing this nitro-glycerine in infusorial earth, wood pulp, or some other porous substance; it is much less dangerous to handle and transport than the pure nitro-glycerine and is very extensively used as an explosive.

Oxides. Ethers.—When we come to study the metals we shall find that two very important classes of their compounds are the oxides and the hydroxides derived from them (just as we have oxides, anhydrides, of the non-metals and the acids derived from them). The hydroxides of the metals are bases and, in some respects, the alcohols, which are also hydroxides, resemble them (*e.g.*, in their reactions with acids). The ethers are compounds which correspond to the oxides—they are oxides of those organic radicals (groups) of which the alcohols are the hydroxides. Thus, we have

$NaOH$ sodium hydroxide	C_2H_5OH alcohol
Na_2O sodium oxide	$(C_2H_5)_2O$ ether

Ethyl ether, $(C_2H_5)_2O$, ordinary ether, sulphuric ether, is made by extracting H_2O from alcohol by means of strong sulphuric acid:

$$2C_2H_5OH = (C_2H_5)_2O + H_2O$$

Ether is a colorless liquid with a strong odor. It boils at about 35° and evaporates rapidly at ordinary temperatures (producing much cold). It is very inflammable, hence mixtures of its vapor and air are explosive. It is a valuable anaesthetic.

Fatty Acids.—Corresponding to the members of the paraffin series, the alcohols and the ethers, we have a series of monobasic acids which are known as the fatty acids because some of the higher members of the series occur in fats.

PARAFFINS	ALCOHOLS	ETHERS	FATTY ACIDS
CH_3H	CH_3OH	$(CH_3)_2O$	CH_2O_2 or $HCHO_2$
C_2H_5H	C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4O_2$ or $HC_2H_3O_2$
C_3H_7H	C_3H_7OH	$(C_3H_7)_2O$	$C_3H_6O_2$ or $HC_3H_5O_2$
C_4H_9H	C_4H_9OH	$(C_4H_9)_2O$	$C_4H_8O_2$ or $HC_4H_7O_2$

The general formula for the series is $C_nH_{2n}O_2$. The lower members are liquids with pungent odors, succeeded by members with unpleasant odors like rancid butter, and the higher members are solids with little odor.

Formic acid, $HCHO_2$.—This is found in red ants (Latin, *formica*, an ant), in stinging nettles, in the poison of the bee's sting, etc.

Acetic acid, $HC_2H_3O_2$.—This is the acid present in vinegar (3 – 6%). It is produced by the partial oxidation of alcohol in dilute solution (wine, cider) due to the growth of a ferment known as "mother of vinegar" (*mycoderma aceti*).

$$C_2H_5OH + 2O = HC_2H_3O_2 + H_2O$$

(This change cannot be brought about by oxygen alone.) Acetic acid is also one of the products of the destructive distillation of wood, whence the name, pyroligneous acid. It is a colorless liquid with a pleasant, penetrating odor and sour taste. The pure acid blisters the skin, causing much pain. It is a typical acid, neutralising bases with the formation of water and salts called acetates.

Propionic acid, $HC_3H_5O_2$. *Butyric acid*, $HC_4H_7O_2$.—The latter occurs in combination with glycerine in butter and free (to a very small extent) in perspiration. It is a liquid of extremely unpleasant odor, something between that of perspiration and of rancid butter.

When organic acids react with organic bases (alcohols), salts etherial (known as esters), are produced. Many of these esters are the flavoring principles of fruits.

The flavor of pineapples is largely due to ethyl butyrate, $C_2H_5 . C_4H_7O_2$; oil of wintergreen is methyl salicylate, $CH_3.C_7H_5O_3$.

Palmitic acid, $HC_{16}H_{31}O_2$, and *Stearic acid*, $HC_{18}H_{35}O_2$.—Most animal and vegetable fats and oils, such as suet, tallow, palm oil, olive oil, are made up almost entirely of the glyceryl salts of these two acids, with the corresponding salts of oleïc acid (which belongs to another series). These salts have been given special names: palmitin, $C_3H_5(C_{16}H_{31}O_2)_3$, stearin, $C_3H_5(C_{18}H_{35}O_2)_3$ and oleïn, $C_3H_5(C_{18}H_{33}O_2)_3$. When these compounds are heated with a solution of sodium or potassium hydroxide, a metathetical reaction takes place, the corresponding salts of sodium or potassium being formed, together with glycerine. For example,

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3NaOH = 3NaC_{18}H_{35}O_2 + C_3H_5(OH)_3$$

The sodium salts are hard soap and the potassium salts soft soap, and they are soluble in water. By adding salt, the soap separates out, as it is not soluble in brine, and the glycerine can be recovered from the remaining liquid by a special process of distillation.

Experiment.—Boil 50 cc. of olive oil (not cotton-seed oil) with 10 gr. caustic soda and 100 cc. water until, on cooling, a cake of soap forms on the surface. If it is desired to separate all the soap from the liquid, add 100 gr. common salt while the solution is still boiling, stir well and allow to cool. The glycerine remains behind in the brine.

There are of course a great many other organic acids besides those mentioned above, for instance:

Oxalic acid, $H_2C_2O_4$, occurs in sorrel, rhubarb, etc., as the acid potassium salt, KHC_2O_4.

Lactic acid, $HC_3H_5O_3$, formed by a fermentation of sugar, and found in sour milk.

Tartaric acid, $H_2C_4H_4O_6$, occurs in grapes, potatoes, cucumbers, etc.

Citric acid, $H_3C_6H_5O_7$, occurs in many fruits, especially lemons, from which it is manufactured.

Malic acid, $H_2C_4H_4O_5$, occurs in many fruits, especially in apples.

Aromatic Compounds.—During the distillation of soft coal in the manufacture of coal-gas, large quantities of tar are produced. From this tar, which used to be considered a rather useless by-product, an enormous number of products have, of late years, been obtained, among others a number of hydrocarbons belonging to what is called the aromatic series, the first member of which is benzol.

Benzol, C_6H_6, benzene.—(Notice the spelling; benzine is another substance; but, unfortunately, writers are not careful enough in the spelling of these two terms and often mix them up.) Benzol is a colorless liquid with a peculiar odor. It burns with a luminous flame, and is used as a solvent for many substances, *e.g.*, sulphur, rubber.

Phenol, C_6H_5OH, carbolic acid.—This is benzol in which one H has been replaced by OH. It is a weak acid in character and is a valuable antiseptic, but, when pure, exerts a strongly corrosive action on the flesh. It is very poisonous.

There are three di-hydroxy-benzols, $C_6H_4(OH)_2$, resorcin, pyrocatechin and hydroquinone; they are all used as developers in photography. Pyrogallic acid, another developer, is a tri-hydroxy-benzel, $C_6H_3(OH)_3$.

It will be noticed that there are three compounds all having the same formula the di-hydroxy-benzols. The differences in the compounds are due to different arrangements of atoms in the molecule. Such compounds, having the same formula but different properties, are called isomeric, or are said to exhibit isomerism.

Aniline, $C_6H_5NH_2$, is prepared from benzol, and is a colorless oily liquid, darkening in the air. It is used in the manufacture of aniline dyes.

Carbohydrates.—This is an extremely important class of compounds, forming a very large part of our food. They produce fat and are the source of our bodily heat and energy. The compounds contain carbon, hydrogen and oxygen, the last two in the same proportion as they exist in water, *i.e.*, two atoms of hydrogen to one of oxygen. (These compounds must not be confounded with the hydrocarbons, which contain no oxygen.)

Glucose, $C_6H_{12}O_6$, dextrose, grape sugar, occurs in sweet fruits and in honey. Large quantities of it are manufactured by heating starch with dilute sulphuric acid:

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6,$$

the acid acting as a catalytic agent. Cane sugar and cellulose (cotton, linen, wood) also yield glucose when treated in the same way. It is a white, crystalline substance, easily soluble in water, and possessing a sweet taste, though not as sweet as sugar. Yeast causes it to undergo alcoholic fermentation.

It is used as an adulterant of syrups and honey, in beer and wine-making, and as a substitute for sugar in the preserving of fruits.

Cane sugar, $C_{12}H_{22}O_{11}$, occurs in the sap of plants, *e.g.*, sugar-cane, beet, maple. In the manufacture of cane sugar, the juice of the cane is squeezed out by means of powerful rolls and after impurities have been removed by various processes, the solution is evaporated down in vacuum pans, *i.e.*, closed vessels from which the vapors are removed by powerful pumps, thus causing the boiling to take place at a lower temperature than it would otherwise, and preventing the darkening of the sugar. The sugar crystallises out from the concentrated solution. Cane sugar is a white, crystalline solid (transparent in large crystals), easily soluble in water and possessing a very sweet taste. If heated carefully, it melts and slowly turns brown, a substance known as caramel being formed. Cane sugar will not ferment, but yeast slowly converts it into glucose which will ferment.

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

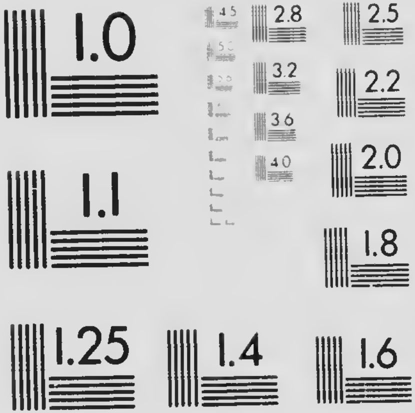
Milk sugar, $C_{12}H_{22}O_{11}$, lactose; occurs in milk of which it forms 3-5%. In the manufacture of cheese, the part of the milk left after the cheese has been removed is called whey ; if this whey be evaporated down, milk sugar crystallises out. It is not as sweet as cane sugar, and is used in making the globules used by homœopathists and for other purposes. Its solution easily undergoes a peculiar fermentation by which it is converted into lactic acid, and this is the cause of the souring of milk. There are a large number of other sugars.

Cellulose, $C_6H_{10}O_5$, forms the walls of plant cells, linen, cotton, etc. It is insoluble in water, but boiling with dilute acids slowly converts it into glucose. Paper consists mainly of cellulose and is made from rags, etc. Wood-pulp is made either by grinding the wood up by means of grindstones (mechanical pulp), or by dissolving out the material (lignin) that cements the cells together, by means of hot solutions of caustic soda or acid calcium sulphite, under pressure (chemical pulp). By the action of nitric acid on cellulose, one, two, or three OH groups are replaced by NO_3 groups. Di-nitro-cellulose, $C_6H_8(NO_3)_2O_3$, dissolved in alcohol and ether, is called collodion; dissolved in camphor, it forms celluloid. Tri-nitro-cellulose, $C_6H_7(NO_3)_3O_2$ is gun-cotton, an extremely explosive solid, used in torpedoes, in blasting and in the manufacture of smokeless powder.

Starch, $C_6H_{10}O_5$, is found in the cells of plants, especially in the seeds, where it is the food stored up for the future use of the baby plant, and in tubers (potatoes) and roots (carrots). Most of our vegetable food consists of this material. The starch occurs in granules in the plants, the shape of the granules being characteristic for each plant; hence, it is often possible to determine the source of vegetable matter by examining the starch grains under the microscope (examination of adulterated pepper, etc.). Starch is a white solid, insoluble in cold water, but rendered soluble by a compound (ptyalin) contained in saliva (hence the need of chewing food and mixing it well with saliva). By boiling with water the granules are burst open and partially dissolved. By heating with dilute acids, starch is converted into glucose. During the germination of seeds, insoluble starch is converted into a soluble sugar; this is what takes place, for instance, in malting grain. In the making of bread, the starch of the flour is partly converted into glucose by the yeast and this glucose then ferments, forming alcohol and CO_2, the latter puffing up the dough. During the baking, most of the alcohol is expelled and the porous dough is rendered harder. If starch be kept at 180–200° for some time it is converted into dextrin (British gum) which is used on the back of postage stamps and for other purposes.

MICROCOPY RESOLUTION TEST CHART

ANSI and ISO TEST CHART No. 2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Proteïds.—There are some very important compounds, such as those that build up our flesh, which are made up of C, H, O, N, S and P, in about the following proportions:

C	52-54 %	N	14-18 %
H	7-8	S	1-2
O	20-25	P	small quant.

The phenomena of life seem to be very intimately connected with these substances: indeed, those parts of plants and animals that do not contain them are really dead matter. Their chemistry is exceedingly complicated, and it is only quite recently that any exact ideas concerning them have been obtained. It is extremely difficult, if not impossible, to be sure that we can obtain them pure, and no formulas have as yet been assigned them. They are the flesh-producing constituents of our food.

Gluten.—If a little ball of dough made from wheat flour be covered with a thickness of cheese-cloth and be then carefully squeezed and kneaded with the fingers under water in a basin, the starch of the flour will pass through the cloth into the water and will settle to the bottom after a time. If the kneading be carried on until no more starch passes out, and the cloth be then opened, a yellowish, gummy mass will be found within, which is mainly gluten. It is not soluble in water. (Fibrin, a constituent of blood, and myosin, one of the constituents of muscle, meat, are similar compounds.)

Legumin is a proteïd that occurs in large proportion in peas, beans, lentils, etc. It is on this account that these vegetables form such a good substitute for meat, which is mainly made up of proteïds, while ordinary vegetables are mainly starch (and water).

Albumens, which occur in the white of egg, in meat and also in the blood and in milk, are soluble in water, but are rendered insoluble—coagulated—by heating to 70°. This is the principal change that occurs in cooking eggs and meat, and is the cause of the formation of the "skin" when milk is heated. Protoplasm, the living part of animal and vegetable cells, is very similar to albumen. (The substances of skin, hair, horns and hoofs are closely allied to the albumens.)

Caseïn occurs in solution in milk. It is not coagulated by boiling, but is by acids (the lactic acid of sour milk, for instance) and by rennet, an extract of the stomach of the calf. It is by this latter method that caseïn is separated from the whey in the making of cheese, which consists almost entirely of this proteïd.

Milk has an average composition of

Water	87.2 %	Caseïn	2.5 %
Milk sugar	5.15	Albumen	0.7
Butter fat	3.75	Ash	0.7

As most of the constituents, except the water, generally vary in quantity as the butter fat does, a determination of this last-mentioned substance is usually sufficient to indicate the value of the milk.

The proteïds are the most important constituents of our food for tissue-building, while the carbohydrates form fat and supply heat and other forms of energy. The value of a food, however, does not depend solely on its content of proteïds and carbohydrates; their digestibility, which depends largely on proper cooking, is a very important factor; moreover, it has been found that the pleasure which attends eating has much to do with the proper digesting of the food.

Alkaloids.—These are vegetable bases made up of C, H, N, and sometimes O. They are very active when taken internally, being generally poisonous, though in small quantities they are most valuable medicinally.

Nicotine, $C_{10}H_{14}N_2$, occurs as the malic acid salt in tobacco leaves. (The brown liquid which condenses in the stems of tobacco pipes and which is sometimes spoken of as nicotine contains little or none of this substance; it is mainly water and tarry matter.)

Morphine, $C_{17}H_{19}NO_3$, is the principal alkaloid of opium, the resinous juice of a certain kind of poppy. It is very valuable in allaying pain.

Quinine, $C_{20}H_{24}N_2O_2.3H_2O$, is derived from the bark of certain Peruvian trees. Its sulphate and chloride are very extensively used in the treatment of fevers.

Cocaïne, $C_{17}H_{21}NO_4$, occurs in coca leaves; its hydrochloride is used to a large extent as a local anæsthetic.

Caffein, or *Thein*, $C_8H_{10}N_4O_2$, occurs in coffee and tea.

Strychnine, $C_{21}H_{22}N_2O_3$, occurs in nux vomica and is used as a heart stimulant in medicine.

QUESTIONS

1. What was the original distinction between organic and inorganic chemistry? Does it still hold? Why?

2. How are the carbon, hydrogen and oxygen in ordinary organic compounds determined?

3. The percentage composition of a compound is: C, 52.18; H, 13.04; O, 34.78. Calculate the formula.

4. The percentage composition of acetic acid is: carbon, 40; hydrogen, 6.7; oxygen, 53.3, and the G.M.V. (vapor) weighs 60 gr. Calculate the formula.

5. The composition of acetylene is: carbon, 92.3%; hydrogen, 7.7%. The G.M.V. weighs 26 gr. Calculate the formula.

6. The composition of benzol is: carbon, 92.3%; hydrogen, 7.7%. The G.M.V. (vapor) weighs 78 gr. Calculate the formula. (*Cf.* quest. 5.)

7. What are hydrocarbons; carbohydrates?

8. What are the chief sources of danger to human life in the case of an explosion of fire-damp in a coal mine?

9. What is a homologous series? Write the formulas of the first five members of the paraffin series and name one of them.

10. What do you know of the chemical composition of petroleum? Is it a definite chemical compound?

11. Name three of the important petroleum products. By what general method are they obtained from the petroleum?

12. Would it be a wise thing to look for the leak in an acetylene generator with a lighted lantern? Why?

13. Compressed acetylene is exceedingly dangerous—Why? And yet we see railway carriages lighted with acetylene coming from strong storage tanks suspended under the cars. Explain.

14. Give an outline of the preparation of coal gas. Mention three important by-products.

15. What is a flame? How do you account for the flame in the case of burning candle-grease?

16. Describe a candle flame, telling what goes on in each of the principal parts.

17. Describe an experiment to prove each of the following statements: (*a*) The inner area of a candle flame consists of a current of inflammable gas; (*b*) in which little or no combustion takes place; (*c*) the luminous area contains particles of solid carbon, and (*d*) burning is going on in it.

18. What is the cause of the luminosity of ordinary flames? Why is the bunsen flame non-luminous?

19. As more and more air is admitted at the base of a bunsen burner, the flame becomes hotter and hotter. What other changes in the flame are connected with this, and how are both related to the total heat produced?

20. Make a drawing of the burner of a blue-flame oil stove and show how it embodies the principle of the bunsen burner.

21. What is the function of the Auer-light mantle? What performed this function before the invention of the mantle?

22. Certain blue-flame kerosene lamps, fitted with Auer-light mantles, are on the market. From a given quantity of kerosene, would you expect these to produce more or less light than is given by an ordinary form of lamp? Why?

23. What substances and what conditions are needed for ordinary combustion? Explain in this connection, the production of smoke.

24. How much air (1/5 oxygen) would be required for the combustion of 100 gr. kerosene (considered to be $C_{14}H_{30}$)? Would "burning" more air increase the total heat produced? Would it alter the temperature of the flame? Why? What would be the result of supplying less air?

25. Carbon dioxide and water vapor are products of the combustion of alcohol. How could you show this? What does it prove as to the chemical composition of alcohol?

26. Why do you think a blacksmith's fire is hotter when the bellows are in use?

27. What are the factors that make the lighting of a candle a slower operation than the lighting of kerosene and still slower than the lighting of gas?

28. If a very hot porcelain dish were held in a candle flame, would soot be deposited on it? Why?

29. Describe the original form of the Davy safety lamp. On what principle does its safety depend? Describe experiments illustrating this principle.

30. Is it possible to manufacture either wood spirit or spirits of wine from wood? Give a brief outline of each process.

31. Methyl alcohol is more expensive to manufacture than ethyl alcohol, and yet a mixture of the two, methylated spirit, can be bought much more cheaply than the pure ethyl alcohol. Why is this?

32. What is the commercial source of glycerine? How is it prepared?

33. To what class of organic compounds does ether belong?

34. Why do we call the fatty acids monobasic—they contain more than one atom of hydrogen in the molecule?

35. What is the chemical composition of fat? How is soap made from it? What sort of chemical action is involved?

36. From what sources may glucose be derived, directly or indirectly?

37. Give an outline of the preparation of sugar (*a*) from sugar-cane, (*b*) from the maple.

38. How may starch be obtained from wheat? How do you think it might be made from potatoes?

39. An average man breathes out about 465 litres of carbon dioxide daily. How much starch could a green plant prepare from this?

40. What are proteïds? Name several of them, mentioning the sources from which they are derived.

41. What substances form the principal portions of our food and clothing? To what class of compounds does each belong?

42. Why are beans such a valuable article of diet?

43. Tell what you know of the composition of milk.

44. As a constituent of food, what is the special value of (*a*) water, (*b*) carbohydrates, (*c*) proteïds?

45. Why is cooking a very important art?

46. Why was Wohler's artificial preparation of urea of great importance?—the substance itself is not of much value.

CHAPTER XVI

SILICON. BORON

Silicon and boron while not, strictly speaking, belonging to the same family, are similar in some of their properties, though the former is tetravalant in all its compounds, being like carbon in this respect, while the latter, boron, is uniformly trivalent.

Silicon occurs in nature in enormous quantities though, unlike carbon, never in the free state. In combination it constitutes about one quarter of the crust of the earth, occurring as the oxide in sand, flint, etc., and in combination with oxygen and many metals in an enormous number of minerals, the silicates (felspar, mica, clay, etc.). It seems to play much the same part in inorganic nature that carbon does in organic. Most plants and animals contain small quantities of silicon.

Silicon in the free state is difficult to prepare and, unlike carbon, is not of much importance. It is interesting to notice, however, that, like carbon, it is an allotropic substance, being known in the crystalline and amorphous forms.

Silicon dioxide, SiO_2, silica.—This, the only oxide of silicon, occurs in nature in enormous quantities and in a great variety of forms. It is called quartz by the mineralogist, and, in the pure state, is colorless and transparent, forming beautiful six-sided prisms terminated by six-sided pyramids (rock crystal). Other varieties, more or less colored by impurities, are agate, amethyst, blood-stone, cairngorm, carnelian, chalcedony, flint, jasper, onyx, quartzite, rose-quartz, sand, sandstone, smoky quartz. Opal is an impure form containing some water. Many of these stones have been known and prized from very early times; some of them are mentioned in the Bible. Curious beliefs are connected with a few of them: for instance, it was held by the ancient Greeks that wine, drunk from an amethyst cup, would not produce intoxication (Greek *a*, un-; *methysis*, intoxication, *i.e.*, unintoxicating).

Silica is hard enough to scratch glass and is unaltered by water and acids (except HF). It is an acid anhydride, but its combination with water must be brought about indirectly. If it is fused with an alkali (NaOH or KOH) or an alkaline carbonate (Na_2CO_3 or K_2CO_3), the corresponding silicate is formed:

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

(Notice the very similar parts played by CO_2 and SiO_2, both acid anhydrides.) The compound is a salt of H_2SiO_3, silicic acid, corresponding to carbonic acid. There are a great many other (hypothetical) silicic acids of which the very numerous silicates found in nature are to be regarded as salts. It is very doubtful whether any silicic acid has ever yet been prepared in the pure state.

Many silicates or mixtures of silicates, artificially produced, are of great practical importance; such are glass, porcelain, earthenware, brick, Portland cement. They will be spoken of later on.

Silicon carbide, SiC, carborundum.—A mixture of sand (SiO_2) and coke is raised to a very high temperature in the electric furnace, when the following reaction takes place:

$$SiO_2 + 3C = 2CO + SiC$$

The slightly impure carborundum thus obtained is brown or black (often exhibiting beautiful iridescent colors) and is very hard, only diamond and one or two other substances surpassing it in this respect. On this account, it is used for grinding and polishing, in the form of powder, wheels, whetstones, etc.

Boron.—Like silicon, boron is never found free in nature; it occurs as boric acid, H_3BO_3, borax, $Na_2B_4O_7.10H_2O$, and some other compounds.

Boric acid, H_3BO_3, boracic acid, occurs in solution in hot springs and natural steam jets in Tuscany and other places. It is a pearly white solid, only slightly soluble in water (4 parts in 100 of water at ordinary temperatures). It is a very weak acid, but has valuable antiseptic properties. On this account its solution is used for bathing wounds, sore eyes, etc., and it causes little or no smarting; it is also employed as a preservative for milk, tinned meats, etc.

Borax, $Na_2B_4O_7.10H_2O$, is found in certain very dry countries, as Thibet and Southern California. It is a white, crystalline solid and is used as a flux in soldering because it has the power, when fused, of dissolving metallic oxides and thus producing a clean surface; it is also employed as a preservative for meats.

QUESTIONS

1. In what respects does silicon resemble carbon?

2. Why is silicon called an allotropic element?

3. N[illegible] few of the forms in which silicon occurs in nature. Describe [illegible] which you have seen.

4. Wh[illegible] the difference between silicon and silica?

5. What is the meaning of the word amethyst? Why was the name applied to this form of silica?

6. To what class of reactions does the one between sodium carbonate and silica belong?

7. Why might SiO_2 be called silicic anhydride?

8. What substances of commercial importance are composed, in part at least, of silica?

9. Why is it a good thing to have a little box of boric acid in the house?

10. Potassium, magnesium and iron (ferric) have valences of 1, 2 and 3 respectively. Write the formulas of their (normal) nitrates, sulphates and borates.

CHAPTER XVII

THE METALS

As has already been seen, the elements are divided into two large groups, metals and non-metals.

Some of the metals have been known from very early times: thus, gold, silver, copper, iron, tin and lead are mentioned in the Old Testament and also in the works of the early Greek writers. Mercury is first mentioned about 350 B.C.

These seven metals were named by the alchemists after the seven members of the solar system which were known to them:

Gold	Sun	Iron	Mars
Silver	Moon	Tin	Jupiter
Copper	Venus	Lead	Saturn
	Mercury	Mercury	

and they were represented by the corresponding astronomical symbols.

Gold and silver were called noble metals, because they were not altered in the fire, *i.e.*, were not oxidised, while the other metals were called base. Malleability was looked upon as the distinguishing characteristic of metals and hence, for a long time, there was some hesitation in admitting mercury to this class of substances. The brittle metals, antimony, bismuth and zinc, when discovered, were classed as semi-metals on account of their small malleability.

Most people to-day have a hazy idea as to what a metal is, but, if asked to put it into words, would not find it a simple task. A careful consideration of the question, however, enables us to make the following statements with regard to this class of simple substances :

1. With the exception of mercury, they are all solid at ordinary temperatures.

2. They all exhibit a peculiar appearance, known as metallic lustre, which is due to the two facts (*a*) that they are very opaque, and (*b*) that they reflect light strongly.

3. They can generally be hammered or rolled out into sheets, and be drawn out into wire ; that is, they are malleable and ductile.

4. They are the best conductors of heat and of electricity.

5. Their oxides are basic anhydrides, and their hydroxides, bases.

The characteristics mentioned under 1, 2, 3 and 4 are physical, that given under 5 is chemical and, therefore, is perhaps the most important of them all to the chemist ; hence, we may state as a definition :

Metals *are base-forming elements.*

When the hydroxide of a metal is dissolved in water, it is electrolytically dissociated in such a way as to yield hydroxyl anions—these are the cause of what is known as basic reaction—while the metal part forms kations. Hence, a metal may be defined as an element capable of forming simple kations.

It must be carefully remembered that the distinction between the metals and the non-metals is by no means sharp ; certain elements form compounds with hydrogen and oxygen that sometimes behave like acids and sometimes like bases, depending on the nature of the other substance or substances present (just as certain people are liberals or conservatives according to the company in which they find themselves).

Certain molecules can break up in such a way as to yield hydrogen ions—(*i.e.*, behave like acids), and also in another way so as to yield hydroxyl ions (*i.e.*, behave like bases). As an example, may be mentioned H_3AsO_3, or $As(OH)_3$, which can dissociate electrolytically into

$$3H^+ + AsO_3^{\equiv}, \quad \text{or} \quad \overset{+}{\overset{+}{As^+}} + 3OH^-$$

Occurrence of the metals.—Naturally occurring substances may be classified into three great groups, often called kingdoms, *i.e.*, animal, vegetable and mineral. All natural substances that are not animal and vegetable, then, are **Mineral**; hence, water, limestone, diamond, flint, air, etc., and all other inorganic substances found in nature, are minerals; and those minerals, a portion of which is useful and can be extracted, are called **Ores** of these useful things.

A mineral is a single chemical substance, elementary or compound; a rock may be made up of a single mineral (marble), or of a mixture of minerals (granite: quartz, felspar and mica).

The metals sometimes occur in the free state (uncombined), or "native," as the mineralogists say. Thus free gold, free copper are found in nature; they are therefore minerals, and we speak of native gold, native copper, etc.

The metals are also found in nature as oxides and as salts—the silicates, carbonates, sulphides and sulphates being the commonest salts.

Metallurgy.—A study of those methods by means of which the metals are commercially extracted from their ores, forms the very important science known as metallurgy. This is a practical, or applied, science; and it is really a branch of chemistry. It is, however, a complex study in itself and hence only a very few of its methods will be referred to in what follows.

More than sixty metallic elements are known and they are generally classified according to what is called the periodic system—something too complicated for us to go into here. Only a few of these metals, however, are of prime importance and they may be classified for our present purpose as follows:

1. Those which are useful chiefly in the form of compounds:
    The metals of the alkalis: Sodium, potassium.
    The metals of the alkaline earths: Calcium, magnesium.

2. Those which are useful as compounds and also in the free state :
   Iron, silver, copper, mercury, zinc, aluminium, tin, lead.
3. Those which are useful chiefly in the free state :
   Gold, platinum.

QUESTIONS

1. What is a metal ?

2. Into what two classes did the alchemists divide the metals? Characterise each class. What did they consider to be the most important characteristic of all metals ?

3. What are the principal physical characteristics of the metals? What the chemical ?

4. What is meant by metallic lustre, malleability, ductility ?

5. Why are telegraph wires made of metal and not of rope ?

6. What are minerals ? What are ores ? Are all minerals ores ? Are all ores minerals ?

7. Would a Canadian call free gold found in California native gold ? Why ?

8. Write a note on metallurgy.

9. Contrast the characteristics of the metals with those of sulphur.

10. To what kingdom does each of the following belong : meat, granite, snow, starch, air, water, horn ?

11. Name five minerals that you are acquainted with.

12. Into what classes may the more common metallic elements be divided ? Mention a few in each class.

CHAPTER XVIII

THE METALS OF THE ALKALIS: SODIUM, POTASSIUM (AMMONIUM)

The hydroxides of the metals of this family are very soluble in water and are the strongest bases that we know. These hydroxides have been long known as the alkalis; hence the metals themselves are called the metals of the alkalis. The elements have a valence of one.

Sodium.—Although compounds of this element have been known and used from time immemorial, the metal sodium was obtained in the free state first in 1807 by the English chemist, Sir Humphrey Davy.

Sodium occurs in nature principally as the chloride, $NaCl$, common salt, and it is mainly from this source that it and its compounds are prepared.

The metal is obtained by decomposing fused sodium chloride (or sodium hydroxide) by means of the electric current, and is silvery-white, as soft as wax and slightly lighter than water. (Density = 0.97.) It tarnishes very rapidly in the air, a thin film of Na_2O and then Na_2CO_3 being formed, and it decomposes water with great energy,

$$Na + H_2O = NaOH + H$$

On these accounts, metallic sodium is generally preserved under kerosene or gasoline, liquids that contain no oxygen.

Sodium forms two oxides, Na_2O, sodium oxide, and Na_2O_2, sodium peroxide. The latter is a powerful oxidising agent and, when treated with water or acids, gives hydrogen peroxide.

$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2$$

Sodium hydroxide, $NaOH$, caustic soda, "concentrated lye," may be prepared by treating a dilute solution of sodium carbonate with milk of lime (calcium hydroxide, which is only very slightly soluble, suspended in water):

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$$

The calcium carbonate, which is insoluble in water, is precipitated, and the solution of sodium hydroxide is filtered off and evaporated to a pasty condition; it is then run into cylindrical moulds, the sodium hydroxide being obtained in the form of sticks.

There are several processes now employed in which sodium hydroxide is obtained by means of the electric current direct from sodium chloride.

Sodium hydroxide is a white crystalline solid. It is very deliquescent and also absorbs carbon dioxide from the air, forming sodium carbonate:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

It has a powerful corrosive action on many animal and vegetable substances, whence its name, caustic soda. It is very soluble in water and is a very powerful base, reacting with all acids and decomposing a great many salts, uniting with their acid radicals:

$$2NaOH + CuSO_4 = Cu(OH)_2 + Na_2SO_4$$

On this account it is used in a great many chemical industries; and, because it reacts with grease to produce soluble soap, it is often used in the household for cleaning purposes.

Sodium chloride, $NaCl$, common salt.—This occurs in nature in enormous quantities both in the solid state, as rock salt, and in solution in salt springs, salt lakes and the sea. Rock salt is mined. In some warm countries, salt is obtained by constructing shallow basins along the margin of the sea and allowing the water to flow into them at high tide; the heat of the sun slowly evaporates the water and, after a time, crystals of salt separate out. These are raked out and piled up to dry in the sun. In some countries, weak brines from salt springs are pumped up and allowed to trickle down over huge stacks of brush wood; this process is known as gradation, or graduation, and in this way a very large surface of liquid is exposed to the sun and warm winds and the solution becomes concentrated enough to allow of its being further evaporated economically by means of heat from fuel. Strong brines are evaporated in pans directly over fires. Crystals of salt are very liable to contain little cavities filled with the solution from which they have separated out (mother-liquor) and this is the cause of the snapping (decrepitation) which takes place when salt is heated.

Pure salt is a white crystalline solid, and is not deliquescent. The uncomfortable habit which table-salt has of getting sticky in moist weather is due to the presence in it of deliquescent impurities, mainly chlorides of calcium and magnesium.

Salt, as has already been said, is the raw material from which most sodium and chlorine compounds are prepared; it is also an essential constituent of the food of man and animals, and is used in preserving meats, fish, butter, etc.

Sodium carbonate, Na_2CO_3, soda, soda-ash.—This compound has for centuries been of very great importance to the human race, as it is employed in the manufacture of hard soap, glass and other extremely useful products. It was formerly obtained from the ashes of certain plants growing on the seashore (as potassium carbonate is obtained from the ashes of ordinary land plants) and from certain natural deposits in Egypt and elsewhere. At the time of the French Revolution the French ports were blockaded and it was impossible for France to obtain from abroad the necessary quantity of this much-needed substance; hence, the Government called upon all those who had processes for the manufacture of soda from common salt to report to the Commission "so as to render vain the efforts and hatred of despots." The Commission reported in favor of the process of an apothecary, Nicholas Leblanc, which thus became public property; and this process with no material alterations is in use to-day. Poor Leblanc, however, died in a French asylum for paupers.

1. *The Leblanc process* involves the following processes:

a. The salt-cake process, in which salt is treated with sulphuric acid, sodium sulphate (salt cake) and hydrochloric acid being produced:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

The gaseous hydrochloric acid is led off and absorbed in water.

b. The black-ash process, in which the salt-cake is heated with carbon (powdered coal), whereby it is reduced to sodium sulphide

$$Na_2SO_4 + 4C = Na_2S + 4CO,$$

and this sulphide is heated with calcium carbonate (chalk, or marble), a metathetical reaction taking place:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

The two reactions just referred to are carried on together, the mixture of salt-cake, coal and chalk being put into a large furnace and stirred. As there is always an excess of coal, the resulting material is dark in color, and hence is called black-ash.

c. The lixiviation process, or separation of the soluble sodium carbonate from the insoluble calcium sulphide. This is effected by placing the black-ash in tanks and treating it with water. The solution of sodium carbonate is run off from the insoluble calcium sulphide (tank-waste), evaporated to dryness and highly heated, the product being Na_2CO_3, *soda-ash*, which is used to an enormous extent in the manufacture of soap, glass, etc.

If soda-ash be dissolved in water and the solution allowed to crystallise, *soda crystals, washing soda*, or *sal soda*, is obtained, $Na_2CO_3 . 10H_2O$.

2. *The Solvay or Ammonia-Soda Process.*—Of late years, a large proportion of the soda of commerce has been made by this process, as the product is purer and cheaper than that made by the Leblanc process.

A very strong solution of salt is treated with ammonia and then with carbon dioxide. These combine with each other and with water thus :

$$NH_3 + CO_2 + H_2O = NH_4HCO_3$$

and the acid ammonium carbonate thus produced reacts metathetically with the sodium chloride :

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$

The sodium bicarbonate, being only sparingly soluble in cold water, is precipitated in the form of minute crystals and is separated from the solution of ammonium chloride by filtration. When it is heated it breaks up as follows :

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

As has already been said, sodium carbonate can be produced from salt better and more cheaply by the Solvay process than by the Leblanc. Why is it then that the Leblanc process has not long ago been abandoned? It is because it produces hydrochloric acid as a by-product, and hydrochloric acid is very much in demand for the manufacture of chlorine and for other purposes. In the superintendence of modern manufacturing plants, a great deal of attention is paid to the working up into valuable by-products of what would otherwise be waste material, and these by-products in many instances are now the chief support of the process, as has just been pointed out in the case of the hydrochloric acid of the Leblanc soda process.

Sodium bicarbonate, $NaHCO_3$, baking soda, "saleratus," is manufactured from salt, as already described, by the Solvay process. It is used in the manufacture of baking powders by mixing it dry with a solid acid, or an acid salt such as cream of tartar (acid potassium tartrate). When water is added, the two compounds react thus:

$$NaHCO_3 + KH(C_4H_4O_6) = KNa(C_4H_4O_6) + H_2CO_3$$
$$H_2CO_3 = H_2O + CO_2$$

Sodium nitrate, $NaNO_3$, Chili saltpeter, Chili nitre.—This compound, which is very easily soluble in water, is found in nature principally in a desert in Chili; smaller deposits of it exist in a few other arid regions. It is separated from the earth and stones accompanying it by dissolving it out in water and evaporating the solution to crystallisation. As it is somewhat deliquescent, it cannot be used in making gunpowder, though much cheaper than potassium nitrate; but it is the source of almost all the nitric acid of commerce and is used very extensively as a fertiliser.

Sodium sulphate, Na_2SO_4, is manufactured in the Leblanc process, and is used in glass making. When crystallised from solution, $Na_2SO_4.10H_2O$, it is called Glauber's salt after its discoverer, and is used in medicine.

Sodium pyroborate, $Na_2B_4O_7.10H_2O$, borax, has already been mentioned.

Sodium silicate, Na_2SiO_3, is called water-glass on account of its solubility. It is used in making artificial stone and for other purposes.

Sodium sulphite, $Na_2SO_3.7H_2O$, is used as a disinfectant, as a preservative and in photography.

Sodium thiosulphate, $Na_2S_2O_3.5H_2O$, "hypo," is used as a "fixer" in photography and also as an "antichlor" to destroy the excess of chlorine after fabrics have been bleached with this last-named substance.

Sodium hypochlorite, $NaClO$, is prepared along with sodium chloride, by passing chlorine into a dilute solution of sodium hydroxide:

$$2NaOH + 2Cl = NaClO + NaCl + H_2O$$

A similar solution is obtained by mixing solutions of sodium carbonate and bleaching powder:

$$Na_2CO_3 + CaCl.OCl = CaCO_3 + NaClO + NaCl$$

The $CaCO_3$ being insoluble separates out and the solution left is known as "eau de Javelle," or Javelle water, and is used for bleaching and cleaning.

Sodium chlorate, $NaClO_3$, may be prepared by passing chlorine into a hot, strong solution of sodium hydroxide:

$$6NaOH + 6Cl = 5NaCl + NaClO_3 + 3H_2O$$

Sodium chlorate and sodium hypochlorite are now manufactured largely by electrical methods.

Sodium and its compounds when introduced into a non-luminous flame, such as that of a bunsen burner, impart to it a strong yellow color. In this way the presence of sodium may often be recognised.

EXPERIMENT.—Heat the end of a piece of platinum wire in the bunsen flame until the flame is no longer colored by any small quantity of impurities adhering to the wire; then dip it into a solution of common salt and heat again. The flame is tinged yellow.

Potassium occurs as the chloride and sulphate in enormous deposits at Stassfurt in Germany, this being, at present, the principal commercial source of potassium compounds. There are somewhat similar deposits, though very much smaller, in some other localities. Further, orthoclase felspar, $KAlSi_3O_8$, is a constituent of granite and many other volcanic rocks, and when these rocks are disintegrated by the weather the potassium passes in a soluble condition into the soil.

The principal reaction in this decomposition of felspar may be represented by the following equation:

$$2KAlSi_3O_8 + 2H_2O + CO_2 = K_2CO_3 + Al_2Si_2O_7.2H_2O + 4SiO_2$$

The hydrated aluminium silicate formed is kaolin, china clay; ordinary clays are this substance mixed with varying proportions of other substances such as silica, iron oxide, etc.

All fertile soils contain potassium compounds and this element is an essential constituent of the food of almost all higher plants. When these plants are burned, the potassium remains behind as K_2CO_3 in the ashes and may be leached out with water in which it is very soluble. When this solution is evaporated down to dryness in a pot, the crude potassium carbonate remains and is known as pot-ash, potash, and potassium is simply a latinised form of this word (hence, only one *t* in potassium).

Potassium is prepared by methods similar to those used in preparing sodium, and the properties of the two metals are much alike. (Density = 0.87.)

The compounds of potassium resemble those of sodium very closely.

Potassium hydroxide, KOH, caustic potash, is very similar to sodium hydroxide in its properties and is prepared by similar methods.

Potassium chloride, KCl, as has already been said, occurs in nature at Stassfurt and elsewhere and is now the source of most other potassium compounds. It is also used as a fertiliser.

Potassium bromide, KBr, is used largely in medicine and in photography, as is also

Potassium iodide, KI.

Potassium chlorate, $KClO_3$, may be prepared in the same manner as sodium chlorate. It is used in the preparation of oxygen, in medicine and in the manufacture of matches, fireworks and explosives.

Potassium carbonate, K_2CO_3, potash, as has already been said, is obtained by lixiviating wood ashes and evaporating the solution. If the crude potash thus obtained be redissolved, the solution filtered and again evaporated, a product called pearl ash, a less impure form of potassium carbonate, is obtained. Potassium carbonate is also manufactured from potassium chloride by the Leblanc process. It is very valuable as a fertiliser and in the manufacture of soft soap and other potassium salts.

Potassium nitrate, KNO_3, nitre, saltpeter (Bengal saltpeter), unlike sodium nitrate, is not deliquescent and its chief use is in the manufacture of gunpowder, which is a very intimate mixture of saltpeter, carbon (charcoal) and sulphur. The principal reaction that takes place when gunpowder explodes is:

$$2KNO_3 + 3C + S = K_2S + 3CO_2 + N_2$$

The gases produced occupy (when cooled) about 280 times the volume of the original powder; the potassium sulphide is a solid and is the principal cause of the smoke produced and the fouling of the gun-barrels.

Saltpeter is formed when animal matters such as manure decay in presence of air and substances (such as wood ashes) containing potassium. The potassium nitrate formed can be extracted by water. Formerly large quantities of it were made in this way. Now, however, it is prepared by mixing hot, strong solutions of sodium nitrate and potassium chloride; the reaction which takes place is

$$NaNO_3 + KCl = NaCl + KNO_3$$

and the KNO_3 is isolated by suitable processes.

Potassium sulphate, K_2SO_4, is found in large quantities at Stassfurt and is used as a fertiliser.

Potassium cyanide, KCN, is used very extensively in the "cyanide" process of extracting gold from its ores. It is extremely poisonous.

Potassium and its compounds tinge the non-luminous flame pale violet. If a very small quantity of sodium compound be present at the same time, however, the strong yellow flame due to the presence of this element entirely obscures the pale violet light due to the potassium. If the flame be examined through a cobalt-blue glass, however, the yellow rays cannot reach the eye and the violet color may then be seen.

EXPERIMENT.—Clean a piece of platinum wire by holding it in a bunsen flame and then dip it into a solution of potassium chloride and hold it in the flame again. Add a drop or two of a solution of sodium chloride to several cubic centimetres of a solution of potassium chloride and examine with the naked eye the coloration of the flame produced; then examine the flame through a piece of cobalt-blue glass.

A better method of analysing the colors of the flame is by means of an instrument called a *spectroscope*, the essential part of which is a glass prism. When light is allowed to pass through such a prism, in the proper way, it is broken up into all its constituent colors, which are arranged in the order in which they occur in the ordinary spectrum. In this way the sodium light and the potassium light would fall in two different places and therefore would not interfere with each other. By means of this instrument it has been possible to discover many of the elements that occur in the sun and in the fixed stars. For further information on the subject, however, a text-book on physics must be consulted.

Ammonium.—When ammonium hydroxide (p. 134) is neutralised with various acids, salts are formed which resemble very closely the corresponding potassium salts obtained by neutralising potassium hydroxide with the same acids. When analysed they are found to contain NH_4 in the place of K; thus, we have

KOH	NH_4OH
KCl	NH_4Cl
KNO_3	NH_4NO_3
K_2SO_4	$(NH_4)_2SO_4$
etc.	etc.

The group NH_4, then plays the part of a metal in all these compounds; it is called a metallic radical and is named ammonium. It has a valence of one, like potassium and sodium.

All efforts to prepare the compound radical by itself have failed so far, a mixture, or rather a gaseous solution, of NH_3 and H being obtained.

Ammonium hydroxide, NH_4OH, has already been described.

Ammonium chloride, NH_4Cl, sal-ammoniac, is obtained by driving the ammonia obtained from gas liquor into a solution of hydrochloric acid:

$$NH_3 + HCl = NH_4Cl$$

It is purified by heating it in an iron pot, when it vaporises without melting and recondenses on the inside of the cover. This vaporisation, of a solid, without melting, and the recondensation of the vapor directly to a solid, is called *sublimation*. Iodine is purified in this way. Ammonium chloride is a white solid, used largely in batteries, in soldering and as a reagent in the laboratory.

Ammonium sulphate $(NH_4)_2SO_4$ is obtained by absorbing the ammonia from gas liquor in sulphuric acid :

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

It is used largely as a fertiliser.

All ammonium salts give off NH_3 when treated with slaked lime and warmed :

$$(NH_4)_2SO_4 + Ca(OH)_2 = CaSO_4 + 2NH_3 + 2H_2O$$

QUESTIONS

1. What are the metals of the alkalis? Why are they so called? In what respects do these metals resemble each other?

2. How does sodium occur in nature? How may it be obtained from this source?

3. What does sodium look like?

4. Why do we call sodium a metal? (Compare it as far as you can with the characteristics of metals given in the preceding chapter.)

5. Mention all the chemical steps by which sodium hydroxide is obtained from common salt.

6. Why is sodium preserved under kerosene or gasoline? Can you suggest any other way of keeping it?

7. What happens to sodium hydroxide when it is left exposed to the air? How should a knowledge of these facts influence us in keeping concentrated lye in the kitchen?

8. Mention four methods of obtaining salt from natural sources. Which do you think they probably do *not* employ at Goderich, Ontario?

9. Why does salt decrepitate when heated? Salt may be fused and then solidified again. Do you think such salt would decrepitate? Why?

10. The term mother-liquor is employed in connection with many other substances than salt: how would you define it?

11. You have doubtless observed that table salt gets sticky on exposure to moist air; and, yet, "the book says" that sodium chloride is not deliquescent. How do you harmonise this fact and this statement?

12. Mention some of the important uses to which salt is put.

13. Mention as many substances already studied as you can that are prepared directly or indirectly from common salt.

14. Can you think of any influence that the French Revolution had on chemistry?

15. What are the different secondary processes that make up the Leblanc soda process? Represent each by an equation or equations, where possible.

16. How are salt-cake and hydrochloric acid separated in the Leblanc process?

17. Assuming that hydrochloric acid (in solution) is worth three cents a kilogram, what is the value of the acid obtained during the conversion of 1,000 kilos of salt into soda-ash? How much soda-ash should be obtained?

18. If a soap maker needs 100 tons of sodium carbonate, would it be cheaper to transport it to him as soda-ash or as soda-crystals?

19. It is stated that soda can be manufactured more cheaply, and purer, by the Solvay process than by the Leblanc process; and yet, the latter is still carried on as well as the former. How do you account for this?

20. What is the general composition of baking powders? How do they act?

21. Why is baking powder used in cookery? Is it used in making bread? Why? (If you cannot answer these questions, consult a cook.)

22. An English king once shouted to his soldiers: "Fear the Lord and keep your powder dry!" Could this advice have been followed if sodium nitrate had been used instead of potassium nitrate in the manufacture of the powder? Why?

23. Water-glass is sometimes used [illegible] housewives. Try to find out for what purpose.

24. What is Javelle water? What is it used for? (Ask your mother.)

25. How would you preserve a specimen of metallic potassium?

26. Why do you think potassium chlorate is used in the heads of some matches?

27. What is the difference between potash and pearl ash? Why do you think Canada produces less of these substances than formerly?

28. Mention an important difference between the ashes of (some) plants growing on the sea-shore and those growing inland.

29. What is the difference between Chili saltpeter and Bengal (ordinary) saltpeter?

30. Why are wood ashes valuable as fertilisers?

31. Can you think of a method for analysing gunpowder?

32. As it is the NO_3 that is the useful portion of one of the constituents of gunpowder, why will not $NaNO_3$ do just as well as KNO_3?

33. What is the valence of sodium, of potassium, of ammonium? How do you know?

34. What is ammonium, ammonia?

35. Why is ammonium called a metallic radical? How may it be prepared in the free state?

36. How could you show that sal-ammoniac contains ammonia?

37. How could you distinguish between sodium chloride and ammonium chloride?

38. How could you distinguish between sodium nitrate and ammonium nitrate?

39. What substances, already studied, are prepared from ammonium chloride, ammonium nitrate?

40. What is the difference between sublimation and distillation? The process by which "flowers of sulphur" is produced is often spoken of as sublimation. Do you consider this to be a correct use of the term? Why?

CHAPTER XIX

THE METALS OF THE ALKALINE EARTHS
CALCIUM. MAGNESIUM

The alchemists spoke somewhat vaguely of a class of substances which they called the "earths," and which were supposed to be elements. These were non-metallic, insoluble in water (or nearly so) and unalterable in the fire; some of them exhibited an alkaline, or basic, reaction when treated with water and litmus and, hence, were known as the "alkaline earths." In 1807 Davy showed that these alkaline earths were not elements, but oxides of the metals barium, strontium, calcium and magnesium.

These elements, barium, strontium, calcium and magnesium, occur largely as carbonates and sulphates and are bivalent. The metals themselves are not of very great importance, but some of their compounds are absolutely necessary to our modern civilization.

All the metals of this group, like those of the preceding family, are prepared by the electrolysis of the fused chlorides.

Calcium.—This element occurs to an enormous extent in nature, the principal compounds being the carbonate and the sulphate.

The metal, which is prepared by the electrolysis of the fused chloride, is silvery white and harder than sodium. Its density is 1.54. It decomposes water, forming $Ca(OH)_2$; in dry air, it is almost unaltered, but, when heated, combines with the oxygen to form CaO, and with the nitrogen to form Ca_3N_2, calcium nitride.

Calcium oxide, CaO, lime, quicklime.—Lime is "burned" by heating calcium carbonate (limestone, marble) to a high temperature, under circumstances which allow of the easy escape of the carbon dioxide formed. This is carried out in lime kilns, which are of various kinds. The simplest are made by constructing a cylindrical or barrel-shaped furnace in the side of a hill, building an arch of limestone a little above the floor and filling in above it with more limestone; a fire is then built under the arch and the following reaction slowly goes on:

$$CaCO_3 = CaO + CO_2$$

When the reaction is complete, the fire is allowed to go out, and the lime is removed from the kiln when it has cooled down sufficiently for a man to go in and take it out. Such a kiln is known as an "intermittent" kiln. Other and larger kilns are "continuous," *i.e.*, work without interruption. They are more or less cylindrical, with several fireplaces built round the sides near the bottom in such a way that the lime can work down the main shaft without falling into them; or they are simple cylinders, the limestone and fuel (generally coke) being fed in together at the top while the lime and ashes are withdrawn at the bottom.

Experiment.—Place a piece of calcium carbonate (limestone, marble) on a piece of moist red litmus paper and notice what happens. Bend the end of a piece of platinum wire round a piece of calcium carbonate and, by this means, hold the latter in the flame of the bunsen burner for a minute or two. When the splinter has cooled, lay it on a piece of moist red litmus paper and notice what happens. Explain.

Pure lime is a white solid which can be melted only in the intensest heat of the electric furnace. In the flame of the oxy-hydrogen blowpipe, it is quite infusible and non-volatile. It reacts energetically with water, combining with it to form the hydroxide:

$$CaO + H_2O = Ca(OH)_2$$

This process is known as slaking (or slacking) and produces so much heat that, if only a little more water is used than is necessary to combine with the lime, the water will boil. Lime will absorb moisture from the air, undergoing exactly the same change as in slaking, and it will also absorb carbon dioxide, thus :

$$CaO + CO_2 = CaCO_3$$

On account of these two reactions, lime exposed to the air gradually crumbles and is found to be converted into a mixture of the hydroxide and the carbonate. Such lime is said to be air-slaked.

Calcium hydroxide, $Ca(OH)_2$, slaked lime.—This is prepared, as already indicated, by treating quicklime with water. When pure, it is a white powder. It is somewhat soluble in water, about 1 part in 600 at ordinary temperatures, and less at high temperatures. (Most other solids are more soluble in hot than in cold water.) The solution is known as lime-water and is used in the laboratory (*e.g.*, as a test for carbon dioxide) and in medicine on account of its mildly basic properties. Slaked lime suspended in water (stirred up with water) is called "milk of lime." Chemically, calcium hydroxide is a base, though not so strong as sodium hydroxide ; it is, however, very much cheaper and hence is used in many industries where a base is required. Both when solid and in solution it reacts with carbon dioxide as follows :

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

EXPERIMENT.—Place a piece of fresh quicklime about the size of a walnut in an evaporating dish and add about an equal bulk of water. Allow to stand and notice what happens. After all action has ceased, rinse the contents of the dish into a large bottle, nearly fill with water, shake well and allow to stand until the liquid becomes quite clear. Carefully pour off this lime-water into another bottle and cork up. The first bottle may then be filled up again with water, shaken, and a fresh supply of lime-water thus prepared.

Taste the lime-water. Test it with red litmus.

Pour some lime-water into a dish and allow to stand exposed to the air for a few hours. Explain the result.

By means of a glass tube, blow through some lime-water.

Mortar is prepared by slaking lime with a slight excess of water and mixing sand with the product. Its hardening takes place in two stages: first, the mechanically mixed water dries out, and secondly, carbon dioxide from the air brings about the reaction just mentioned above. This naturally takes place very slowly, as the supply of carbon dioxide is small. Sometimes we see coke fires built in fire-baskets in freshly plastered houses, the heat from them hastening the drying of the mortar and the carbon dioxide they supply accelerating the conversion of the calcium hydroxide to calcium carbonate. The sand in the mortar serves to keep it porous, so that the carbon dioxide can penetrate it, and it also prevents excessive shrinkage on drying and hardening.

Certain limestones contain a considerable proportion of silica, and then when burned give "hydraulic" limes, that will set under water. This will be considered further on, under Portland cement.

Calcium carbonate, $CaCO_3$.—This occurs in enormous quantities in nature. As limestone, marble and chalk, it forms mountain ranges and underlies great stretches of country; of course, these rocks often contain large proportions of impurities. Shells, chalk, coral, stalactites and stalagmites are other forms of calcium carbonate. The naturally occurring pure compound is called calcite by mineralogists. Iceland spar is a transparent variety. (The so-called chalk used to-day for black-board crayons is frequently not calcium carbonate at all, but some other white soft substance.)

Calcium bicarbonate, $CaH_2(CO_3)_2$.—As has already been said, carbon dioxide is produced during decomposition and decay of vegetable matter, and also in many places is given off from fissures in the earth. Hence, a great many natural waters contain this substance in solution—or rather in combination, as carbonic acid, H_2CO_3.

$$H_2O + CO_2 = H_2CO_3$$

When such water comes into contact with any form of calcium carbonate, such as limestone, the following reaction very slowly takes place :

$$H_2CO_3 + CaCO_3 = CaH_2(CO_3)_2$$

The calcium bicarbonate formed is the acid calcium salt of carbonic acid, and is quite soluble in water, while the normal carbonate is not. The reactions given above are reversible, that is, they can take place also in the other direction, and this happens whenever the carbon dioxide which is then produced can escape ; it is moreover hastened very much by heating the solution. In many places, waters containing this calcium bicarbonate in solution drip slowly from the roofs of caves. As each drop hangs, before falling, a little carbon dioxide goes off into the air and a corresponding tiny quantity of $CaCO_3$ separates out and sticks to the point from which the drop is about to fall. In this way long icicle-like pendants of calcium carbonate are gradually formed, and they are called stalactites. Often a similar sort of action goes on at the floor of the cave where the drops fall, a conical body, called a stalagmite, being slowly built up. In time, the stalactite and the stalagmite may meet and form a natural pillar. We often read of caves containing numbers of these beautiful structures. Sometimes tiny stalactites are seen hanging from the under side of stone bridges.

EXPERIMENT.—Place some lime-water in a beaker and bubble carbon dioxide through it slowly for several hours. Notice the precipitate formed at first and that it afterwards redissolves (at least partially). Explain this. Pour off some of the clear part and boil in a beaker. A precipitate of calcium carbonate is formed. Explain this. Try making a lather with soap in the rest of the clear solution.

Calcium sulphate, $CaSO_4.2H_2O$, gypsum, alabaster.—This is a white crystalline solid and occurs abundantly in nature. It is slightly soluble in water. It is often used in the powdered form as a fertiliser. When very carefully heated (to about 115°) it loses three-quarters of its water of crystallisation:

$$2(CaSO_4.2H_2O) = H_2O.2CaSO_4 + 3H_2O$$

The product is very easily powdered and is known as plaster of Paris. When it is moistened with water, the reaction just given is reversed, and the mass soon becomes very hard, gypsum being formed. Plaster of Paris is extensively used for making casts of statuary, etc., for hard-finishing plastered walls, as a cement, etc.

Experiment.—Shake up some finely divided gypsum in a large bottle with about a quart of water. After shaking a good many times and allowing to stand, pour off the solution. Boil a little of it, and wash the hands with soap in the rest.

Hard water.—Many natural waters will not make a lather with a small quantity of soap, and they are then called hard waters. The cause of the hardness is generally the presence in these waters, in solution, of calcium bicarbonate, or calcium sulphate, or both. (Certain other salts have similar effects.) The reason why these waters behave as they do towards soap, is as follows: As has already been pointed out, ordinary soaps are sodium or potassium salts of certain fatty acids, and are soluble in water. The calcium salts of these acids, however, are insoluble; hence, when soap is added to a hard water, such a metathetical reaction as the following takes place:

$$2NaC_{16}H_{31}O_2 + CaH_2(CO_3)_2 = Ca(C_{16}H_{31}O_2)_2 + 2NaHCO_3$$

The insoluble lime soap separates out as a sticky curd which adheres to the hands or anything else that is being washed and, of course, very much interferes with the cleansing process. Moreover, the withdrawal of soap from solution in this way prevents the water from forming a lather till a quantity of soap in excess of the lime salts in solution has been added. Indeed, the degree of hardness of a water is generally determined by finding out how much of a solution of soap of standard strength is required to just produce a lather with a certain volume of the water under examination.

As has been explained above, calcium bicarbonate in solution is rapidly decomposed when the solution is boiled; hence, a hard water, whose hardness is due to calcium bicarbonate, would be rendered soft by boiling, the calcium separating out as insoluble calcium carbonate and thus in a condition in which it does not react with the soap. Such a water, whose hardness is removed by boiling, is said to be temporarily hard (or to possess temporary hardness). On the other hand, calcium sulphate is not affected by boiling its solution, and hence water whose hardness is due to the presence of this compound is called permanently hard (or possesses permanent hardness).

As hardness in water is very troublesome in a great many processes, it is frequently necessary to soften hard water by chemical means before it is used. Temporary hardness may be removed by the action of slaked lime, thus:

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$

while permanent hardness may be removed by the addition of sodium carbonate:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

In both cases the calcium is precipitated as insoluble calcium carbonate, which may be removed by settling or filtration; the sodium sulphate produced in the second reaction remains in solution but its presence is generally not objectionable. Water is often softened in these ways on the large scale for industrial purposes, huge "softeners" working continuously and in some cases treating as much as 2,500 gallons per minute, being employed.

When temporarily hard water is boiled—as in steam boilers or kettles—the calcium carbonate generally separates out, mixed with other impurities, as a more or less adherent coating called boiler-scale (or "fur").

Calcium silicate.—As was mentioned under silicon, there are a great many silicic acids (H_2SiO_3 is the simplest) and hence there may be a great many calcium silicates. While none of these are of any importance alone, they form very important constituents of glass and Portland cement.

Glass has been known from very early times. Flinders Petrie has discovered remains of glass-furnaces and workshops at Tel-el-Amarnes in Egypt, which date back to 1400 B.C. Glass is not a definite chemical compound, but is to be regarded as a solid solution of various compounds in one another. Ordinary transparent, colorless glass is made by fusing together sand, lime and soda (carbonate or sulphate) in special furnaces. The resulting material has a composition which is represented approximately by the formula $Na_2O.CaO.6SiO_2$, though, as already stated, it is not one compound. After having been thoroughly fused, the glass is blown, moulded, or cast into the articles desired. To blow a bottle, for instance, a certain quantity of the sticky fused glass is collected on one end of an iron pipe; this lump is inserted into a mould the shape of the outside of the bottle desired and the air blown through the iron pipe so as to expand the glass till it fits the mould tightly, when the pipe is broken away. The mould is then opened and the hot but moderately hard bottle removed and the top of the neck finished off. The bottle is now exceedingly brittle and must be annealed. For this purpose, it is placed in a large furnace and heated up to a temperature just short of softening and then cooled *very* slowly. In this way the glass is rendered very much less brittle. Ordinary window glass is made by blowing long hollow cylinders (without using any moulds), cutting off the ends, slitting the open cylinders lengthwise (longitudinally), softening the slit cylinders in a furnace, opening them out flat and annealing the sheets thus produced. Imitation cut glass bowls, etc., are moulded or pressed without being blown. A proper quantity of hot glass is dropped into the mould representing the outside of the bowl, and then the mould for the inside is inserted by a machine and considerable pressure exerted so that the glass is squeezed into shape. It is then annealed. Plate glass is cast in flat slabs by pouring molten glass on to a suitable table with a raised edge and running a heavy roller over it. It is then annealed and both surfaces are ground and polished.

By introducing substances other than lime, soda and silica, different sorts of glass are produced which may be transparent or opaque and of almost any color desired.

Portland cement.—A great many different kinds of cements have for centuries been used for structural purposes, but by far the most important to-day is Portland cement. (It got its name on account of its resemblance, when set, to stone quarried at Portland, England.) It is manufactured by grinding limestone and dried clay to very fine powders, mixing these in just the right proportions, "burning" this mixture till it is partly fused, and grinding the "clinker" thus obtained to a very fine powder. The material thus produced has the property, when mixed with water, of combining with it and setting to a very hard mass, and this it will do even when under water, which of course mortar will not.

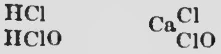
There has been, and still is, a great deal of discussion as to the real chemical nature of cement and its setting. The most recent (the simplest) view seems to be that the important constituent of the cement is a calcium silicate having the formula Ca_2SiO_4, and that the setting is due to water reacting with this to produce a compound containing water of crystallisation, thus :

$$2Ca_2SiO_4 + 7H_2O = 2CaSiO_3.5H_2O + 2Ca(OH)_2$$

Cement is used to an enormous extent to-day as a substitute for ordinary mortar, even in places that are not wet, in all sorts of hydraulic construction and in the making of artificial stone and concrete.

Calcium chloride, $CaCl_2$, is obtained as a by-product in many technical industries. It is an extremely deliquescent substance and, on this account, is much used on the small scale as a desiccating agent, for extracting moisture from gases. It is interesting in that it is a by-product for which, although it is produced in enormous quantities, almost no use has been found, though a very great deal of time and trouble have been spent in trying to find uses for it.

Bleaching powder, $CaOCl_2$, chloride of lime.—This compound is prepared by passing chlorine over slaked lime. $Ca(OH)_2 + 2Cl = CaOCl_2 + H_2O$. It is supposed to be a double salt formed, theoretically, from a molecule of HCl and a molecule of HClO by replacing the two H's with an atom of the divalent calcium:



$$\begin{matrix}HCl\\HClO\end{matrix}\qquad Ca\begin{matrix}^{Cl}\\_{ClO}\end{matrix}$$

When treated with an acid, Cl is evolved:

$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2$$

Even the carbon dioxide of the air brings about a similar reaction:

$$CaOCl_2 + CO_2 = CaCO_3 + Cl_2$$

Bleaching powder, as its name implies, is used in bleaching and also in disinfecting.

Calcium phosphate, $Ca_3(PO_4)_2$, occurs in nature as the mineral phosphorite and is the principal constituent of bones. It, and the acid salt, $CaH_4(PO_4)_2$, have already been spoken of under fertilisers.

Calcium carbide, CaC_2.—This compound is prepared by heating a mixture of lime and coke to an exceedingly high temperature in the electric furnace:

$$CaO + 3C = CaC_2 + CO$$

It is used in the production of acetylene, water reacting with it as follows:

$$CaC_2 + H_2O = CaO + C_2H_2$$

Of course the CaO produced in this reaction is slaked by more of the water present.

Compounds of calcium, if at all volatile, color the non-luminous flame brick red.

EXPERIMENT.—Clean a piece of platinum wire in the flame, dip it into a solution of calcium chloride and heat again. Observe the brick red color of the flame. Hold a piece of quicklime in the flame by twisting the end of the platinum wire round it. The flame will not be colored, because the lime is not volatile—the chloride is.

Magnesium.—This element occurs to an enormous extent in nature, as the carbonate, magnesite, and with calcium carbonate as dolomite, $CaCO_3.MgCO_3$.

The metal may be prepared by electrolysis of the fused chloride, as has been the case with all the metals so far discussed (though in this case carnallite, $KCl.MgCl_2.6H_2O$, is generally the starting point). Magnesium is a silver-white metal, not quite twice as heavy as water (density = 1.75); it is attacked by air only very slowly, the oxide, MgO, being formed. When highly heated, it burns in air with the production of an intense white light, much used in photography. ("Flash lights" are mixtures of powdered magnesium with oxygen-producing substances such as potassium chlorate.)

Magnesium oxide, MgO, magnesia, resembles lime in many ways, though it is still more difficult to fuse. It is practically unaffected in the air.

Magnesium hydroxide, $Mg(OH)_2$, is formed very slowly by the action of water on magnesia. It is only very slightly soluble in water, but its solution has [illegible]lkaline reaction.

[illegible]*ium chloride*, $MgCl_2$.—This compound exists in sea water and other nat[illegible]aters. On boiling its solution, a reaction called hydrolysis, the opposite o[illegible] neutralisation, takes place to a slight extent, whereby magnesium hydroxide is precipitated and hydrochloric acid liberated:

$$MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl$$

If this occurs in boilers, the magnesium hydroxide forms a very objectionable, tightly adhering scale, and the free hydrochloric acid attacks the metal of the boilers and corrodes it. Magnesium chloride is even more deliquescent than calcium chloride, and it is the presence of minute quantities of these two compounds that makes ordinary table salt deliquescent.

Magnesium sulphate, $MgSO_4.7H_2O$, occurs in solution in many mineral springs, especially that at Epsom in England, whence its name of Epsom salt. It is used in medicine and in several of the industries.

Magnesium silicates.—Many of these are known, such as serpentine, soapstone, asbestus, meerschaum, etc.

Magnesium nitride, Mg_3N_2, is formed by heating magnesium in nitrogen. On addition of water it reacts thus:

$$Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$$

Magnesium and its compounds impart no characteristic color to the non-luminous flame.

Barium and **Strontium** resemble calcium closely and are not very common elements. Barium sulphate, which occurs in nature as barite, or heavy spar, and is also prepared artificially, is used as a white pigment and for "weighting" paper. Strontium hydroxide is used in connection with the refining of sugar. Compounds of barium tinge the flame green and those of strontium crimson; on this account they are often used in the making of fireworks, etc.

QUESTIONS

1. What are the alkaline earths?
2. Why was lime classed as an alkaline earth?
3. Write equations representing the reactions that take place between calcium and air, and calcium and water.
4. Describe two forms of continuous kiln. What do you think is the advantage or disadvantage of each?
5. Occasionally a tramp, who has slept beside a lime-kiln, is found dead there in the morning. What do you suppose killed him?
6. What is the difference between an intermittent and a continuous kiln? Describe an example of each.
7. Mention one of the uses of lime depending on its infusibility.
8. Some lime has been stored for several months in a shed. Do you think it will be good? Why?
9. To what class of compounds does calcium oxide belong? Calcium hydroxide, calcium carbonate?
10. Mention a solid that is more soluble in cold than in hot water. Is this phenomenon common?
11. Lime-water is often given to babies and invalids who would be injured by any free acid in the stomach. Can you suggest the reason for this?
12. What is the difference between lime-water and milk of lime? Why do you think the latter is so called?
13. Why do freshly-plastered walls give out water for such a long time?
14. What is the difference between the action of carbon dioxide on quicklime and of carbon dioxide on slaked lime?
15. What is the difference between ordinary lime and hydraulic lime?
16. Carbon dioxide is bubbled through lime-water for a long time. The solution first turns milky, but afterwards becomes clear again. On boiling the clear solution, it again becomes milky. Explain these changes, giving equations for the reactions involved.
17. Show by means of formulas why calcium bicarbonate is said to be the acid calcium salt of carbonic acid.

18. Explain the formation of little stalactites on the under side of stone bridges. Can you think of any kind of stone bridge where it would be quite useless to look for such structures?

19. What is meant by a reversible reaction? Mention two such reactions, and point out why each sometimes proceeds in one direction and sometimes in another.

20. How much water must be mixed with one pound of plaster of Paris in order to set it? With one pound of lime to slake it?

21. How is hard water formed in nature (two methods)?

22. What is temporary hardness and what is permanent hardness in water?

23. A certain water exhibits both temporary and permanent hardness. Can you think of a method by which the degree of each might be determined?

24. Mention two methods by which temporary hardness may be removed, and one by which permanent hardness may.

25. What is meant by annealing in glass manufacture, and why is it done?

26. What are the principal steps in the manufacture of Portland cement?

27. It has been said that the setting of mortar and the setting of cement are opposite chemical actions. Can you explain what is meant?

28. In what way is the setting of cement similar to that of plaster of Paris?

29. What is concrete? What is reinforced concrete? (Ask an engineer.)

30. Why does bleaching powder generally smell slightly of chlorine?

31. Why do you think the lime-light is not red?

32. By consulting the text, arrange the following metals in the order of their densities: calcium, potassium, sodium, magnesium.

33. What is hydrolysis? Give an example.

34. Mention two reasons why you think sea-water unsuitable for use in steam boilers.

35. By what general method are sodium, potassium, calcium and magnesium prepared? What is the action of each (*a*) on air, (*b*) on water?

36. A little pile of magnesium powder is ignited. After all action has ceased and it has cooled, the resulting material is thrown into water. The odor of ammonia is perceived. Account for this. What does it teach with regard to the composition of the air?

CHAPTER XX

IRON. NICKEL. COBALT

Iron is the most important of all the metals and its use by man extends far back into antiquity. It was probably obtained from its ores first in India, and both the Assyrians and Egyptians used iron tools hundreds of years before the beginning of the Christian era. Furnaces for smelting it are mentioned in the Pentateuch, and Homer speaks of iron.

It does not occur native on this earth, except in very minute quantities; but many meteorites are made up largely of it, always associated with nickel and cobalt.

The principal ores of iron are hæmatite, or specular iron, Fe_2O_3; bog iron, or limonite, $2Fe_2O_3.3H_2O$; magnetite, Fe_3O_4; and siderite, or spathic iron, $FeCO_3$. Iron pyrites, pyrite, FeS_2 (fool's gold), although occurring in large quantities, is used more as an ore of sulphur in the sulphuric acid manufacture, than as an ore of iron.

The smelting of iron is the most important of all metallurgical operations. It is carried on on an enormous scale in huge furnaces, called blast furnaces, usually about 80 feet high, though larger and smaller ones are also employed. The general construction of such a furnace is seen in the sketch. The walls are generally made of steel plates and the whole is lined with the best quality of fire-brick. The top is closed by a "cup and cone" (A), the latter being movable, and there are openings at the sides (B) connected with a large pipe for carrying off the furnace gases. Near the bottom are openings (C) called tuyers, through which the blast is forced and two other openings (D) and (E), through which the molten slag and molten metal run, respectively.

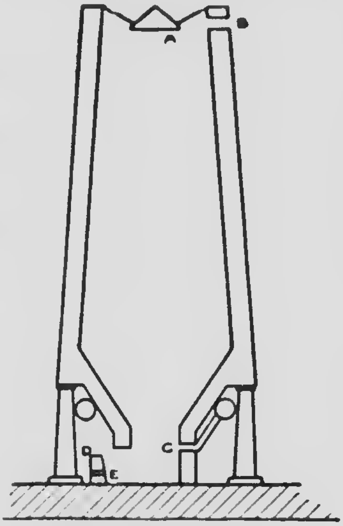


FIG. 27.

Three things are introduced through the cup and cone: ore, fuel and flux. First, the ores which have been roasted, *i.e.*, highly heated in a current of air and gases from burning fuel, to rid them of any water, carbon dioxide, etc., which they [illegible] contain, are the substances from which the metal is produced; secondly, the fuel which is generally coke (*i.e.*, impure carbon) serves a double purpose: (*a*) it burns fiercely, producing intense heat and forming carbon monoxide; and then (*b*) more of the fuel as well as the carbon monoxide act as reducing agents, taking up the oxygen of the ores:

$$Fe_2O_3 + 3C \quad = 2Fe + 3CO$$
$$Fe_2O_3 + 3CO = 2Fe + 3CO_2;$$

and thirdly, the flux is added to combine with the impurities in the ore and fuel to produce an easily fusible, glassy substance called slag. Near the bottom of the furnace, a fourth thing is introduced, the blast, and this is air, generally highly heated, to make the fuel burn rapidly and produce a high temperature.

Three things are withdrawn from the furnace: the furnace gases from near the top, consisting mainly of carbon monoxide, carbon dioxide and nitrogen; and two things from the bottom: the slag already referred to and the metal. This last is run out and cast into bars called pigs, the metal itself being known as pig iron. The furnace gases contain a sufficient proportion of carbon monoxide to burn and are used for heating the blast, in gas engines, etc.

There are three different forms in which iron comes on to the market: cast iron, wrought iron and steel; and the differences are due to the presence of several impurities in the iron in varying amounts.

Cast iron is the product of the blast furnace and it is hard and brittle. It cannot be welded, nor can it be bent to any extent without breaking. It contains from 92 to 94% of iron, the rest being mainly carbon and silicon. It is easily melted and is used for making castings. Spiegel iron is a sort of cast iron containing a great deal of manganese (iron ores containing manganese are used in its production) and a high percentage of carbon.

Wrought iron is made by the *puddling process*, which consists in burning the impurities out of cast iron as completely as possible, the oxides of carbon going off in the form of gas and the oxides of the other impurities forming a slag. The process is carried out in a reverberatory furnace — a sort of saucer-shaped bed over which flames from a fire sweep (Fig. 28). The bed is lined with oxide of iron, which gives up its oxygen to the impurities. The cast iron is melted in this furnace and the oxidation is hastened by stirring up the molten charge with iron rods (puddling). As the iron becomes purer it gets stiffer, because wrought iron melts at a much higher temperature than cast iron. Finally, when the carbon

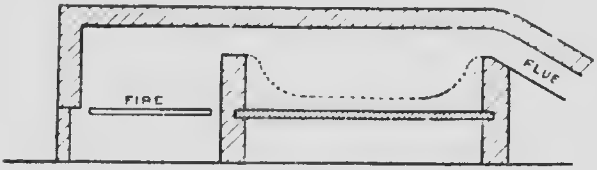


Fig. 28.

content has been reduced to 0.15%, or less, the iron is withdrawn in great lumps and freed from slag by means of the steam hammer or by rolling. Wrought iron is very tough, has a very high melting point and can be welded, *i.e.*, two pieces can be softened in the fire and then joined by hammering or squeezing.

Steel is chemically intermediate between cast iron and wrought iron, and is prepared in several different ways. In the *Siemens-Martin, or open hearth* process, pig iron is melted in a furnace very similar to the puddling furnace described above, except that no iron oxide is used in the bed; scrap iron is added to the charge and the whole melted down. The carbon and other impurities are slowly burned out by the excess of air in the flame, but the process is not carried as far as in the case of wrought iron, about 0.2 to 0.6% of carbon being left. The charge, which remains molten, is then tapped off. Another method of arriving at the same result is the *Bessemer process.* Here the molten pig iron is run into a pear-shaped vessel, called a converter (Fig. 29), and air is blown through it. The carbon, silicon, etc., are burned out practically completely, and then a certain quantity of Spiegel iron is run in which, being very rich in carbon, brings this constituent up to the desired proportion in the whole mass. The converter is then tipped up and the charge poured out. The finest quality of steel, that used for tools, razors, cutlery, etc., is made by the *cementation process.* Bars of the purest wrought iron are packed into huge fire-clay boxes along with charcoal in

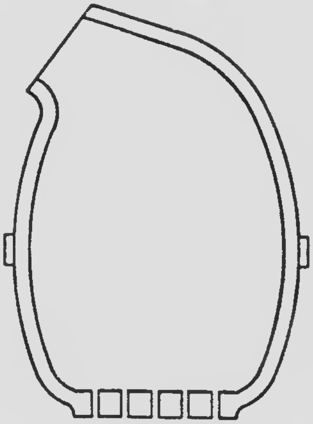


Fig. 29.

little pieces. These boxes are closed and then heated for several days, the carbon slowly combining with the iron. The bars are then taken out, broken up and melted in crucibles, the result being crucible, or cast, steel.

From what has been said, it will be seen that the three different varieties of iron owe their differences mainly to the presence of varying proportions of carbon; wrought iron is nearly pure iron, its carbon content being less than 0.15%; steel contains carbon ranging from 0.2 to 1.5%; and cast iron, still more. However, the different varieties shade into one another, and are not in any sense to be regarded as allotropic forms of the element.

A few typical analyses, from Thorpe's "Dictionary of Applied Chemistry," will serve to illustrate the composition of the various forms of iron:

	PIG IRON	SPIEGEL IRON	WROUGHT IRON	SIEMENS STEEL	TOOL STEEL
Iron	93.46	86.74	99.29	98.49	98.58
Carbon	3.14	5.04	0.10	0.58	1.15
Silicon	2.16	0.41	0.13	0.23	0.17
Manganese . . .	0.50	7.57	0.08	0.64	0.10
Phosphorus . .	0.63	0.16	0.35	0.03	—
Sulphur	0.11	0.08	0.05	0.03	—

If steel be suddenly cooled by dipping it when red-hot into water, for instance, it is rendered hard enough to scratch glass, but is very brittle. This is called hardening. If this very hard steel be then carefully reheated to a certain temperature (depending on the hardness desired) and again quenched, its hardness may be reduced to any desired extent and its toughness correspondingly increased. This is called tempering.

Pure iron is almost silver white in color and has a specific gravity of 7.8 (water = 1). It is very ductile and malleable and is magnetic. When exposed to moist air, or to water containing air, iron rust is formed, $2Fe_2O_3.Fe(OH)_2$. When highly heated in air or in steam, Fe_3O_4, the magnetic oxide, or hammer scale is formed. Iron is soluble in most acids, ferrous salts being formed.

Oxides of iron.—Iron forms several oxides. Ferrous oxide, FeO, is not of much importance. Ferric oxide, Fe_2O_3, is found in nature as the mineral hæmatite, one of the principal ores of iron. When prepared artificially (from ochres, etc.), it is red and is used as a pigment (often in painting bridges, etc.). Magnetite, or magnetic oxide, Fe_3O_4, may be regarded as a compound of the other two oxides; it is attracted by the magnet, whereas the other two are not. It occurs in large quantities in nature and is occasionally found magnetised—it is then called lodestone (leading-stone) because, if suspended, it will act as a compass. It is also formed artificially as hammer-scale.

Iron forms two distinct series of salts corresponding to ferrous and ferric oxides, those in which the iron atom has a valence of two, called *ferrous salts*, and those in which the iron atom has a valence of three, called *ferric salts*.

FeO	ferrous oxide	Fe_2O_3	ferric oxide
$FeCl_2$	ferrous chloride	$FeCl_3$	ferric chloride
$FeSO_4$	ferrous sulphate, etc.	$Fe_2(SO_4)_3$	ferric sulphate, etc.

Ferrous sulphide, FeS, is formed by fusing together iron and sulphur. It is used in the preparation of sulphuretted hydrogen.

Ferrous sulphate, $FeSO_4.7H_2O$, green vitriol, copperas, is prepared on a large scale and is used in dyeing. It is also used in the manufacture of ordinary writing ink which generally contains ferrous sulphate, tincture of galls, gum arabic and water.

Ferric hydroxide, $Fe(OH)_3$, is obtained as a bulky reddish-brown precipitate by adding ammonium hydroxide to the solution of any ferric salt.

Nickel and **Cobalt** are two elements that resemble iron closely in properties. They occur only in small quantities in nature.

Nickel takes a high polish and is acted on by moist air only very slowly, and hence is used for plating other metals such as iron. It is also used in alloys. Nickel coins contain 3 parts of copper and 1 of nickel; German silver contains 2 parts of copper, 1 of zinc and 1 of nickel.

Cobalt compounds are used in the manufacture of "smalt," a blue pigment, and blue glass.

QUESTIONS

1. Calculate the percentage of iron in each of the principal ores.

2. What is the composition of pyrites? As an ore of what substance is it principally used?

3. Describe the blast-furnace, with a sketch. State in tabular form what substances are put in at the top and what near the bottom, with the purposes of each; also, what substances are taken out at the bottom and what at the top with the use of each, as far as possible.

4. What are the principal chemical reactions involved in iron smelting? Give equations where possible.

5. Mention one of the by-products of the blast-furnace process that was originally wasted, but is now utilised.

6. What effect do you think heating the blast has?

7. What are the principal impurities in cast-iron? What becomes of each during the puddling process?

8. What do you think becomes of the iron from the oxide of iron in the bed of a puddling furnace?

9. Compare the puddling process and furnace with the open-hearth process and furnace. Can you think of any reasons for the differences?

10. A Bessemer converter after the "blow" contains ten tons of pure iron. How much Spiegel, containing six per cent. of carbon, must be added to produce a steel containing 0.4% of carbon?

11. What is meant (*a*) by hardening and (*b*) by tempering of steel? (If possible, get a blacksmith to show you the process.)

12. How is magnetic oxide of iron produced artificially? What is its common name when so produced?

13. How do you account for the fact that iron forms two series of salts? Write the formulas of ferrous and ferric hydroxides.

14. For what purpose have we already employed ferrous sulphide? How may it be prepared?

15. What is the composition of ordinary writing ink? What is the pigment used in printer's ink? (Ask a printer what else is in his ink.)

16. Would United States nickels (five-cent pieces) give a fairly pure solution of nickel nitrate when dissolved in nitric acid? Why?

17. Mention any uses for cobalt or its compounds that you know of.

CHAPTER XXI

SILVER. COPPER. MERCURY

The three metals dealt with in this chapter are not very closely related, but have a few characteristics in common. They all occur free, or native, and also in the form of sulphides; they are all very useful both as metals and in the form of compounds; and they all exhibit a valence of one in compounds; copper and mercury also exhibit a valence of two in other compounds.

Silver is one of the metals that has been known from earliest times, as it occurs native, and is easily worked. The alchemists called silver Luna, the moon, on account of its color, and often represented it by the symbol of the crescent.

Besides being found native, silver occurs in the form of various compounds, especially the sulphide, Ag_2S, argentite. Most lead ores contain silver, as do also many copper ores.

The metallurgy of silver is complicated and need not concern us here.

Silver is pure white in the massive condition, but when very finely divided is nearly black; it can be highly polished. Its density is 10.5; it is very ductile and malleable and is the best conductor of heat and electricity known. It is unacted on by air, or water, or both, even at high temperatures and hence was called a noble metal by the alchemists. Most acids do not affect it in the cold, but it is easily soluble in nitric acid even at ordinary temperatures.

Pure silver is too soft to be used for coinage, hence it is alloyed with a little copper which makes it much harder. So-called sterling silver in the British Empire is 92.5% silver and 7.5% copper (in other countries it is 90% silver). Silver ornaments often contain only 80% silver. So-called oxidised silver is silver with a film of black silver sulphide, Ag_2S, on it.

Mirrors are now made by flowing a solution containing silver nitrate with some reducing agent, such as glucose, on a clean surface of glass, when metallic silver is slowly deposited as a bright film adhering strongly to the glass.

Metallic articles may be electroplated with silver by hanging them in a solution of silver and connecting them to the negative pole of a battery, while a plate of pure silver connected to the positive pole dips into the same solution.

Silver nitrate, $AgNO_3$, is obtained by dissolving silver in nitric acid:

$$Ag + HNO_3 = AgNO_3 + H$$

(the hydrogen enters into further reactions with more of the nitric acid present, as is explained under nitric acid). The compound is very soluble in water, and, as black, finely divided metallic silver is very easily obtained from it by the action of reducing agents such as organic matter, it is often used in the preparation of marking inks. Cast into sticks, it is called "lunar caustic"—lunar, from the old name for silver; caustic, on account of its destructive action on flesh, etc. (In contact with organic matter, it practically gives up nitric acid, which attacks the organic matter.)

EXPERIMENT.—Place a five-cent piece in a test-tube and add about one cubic centimeter of nitric acid. The coin will be dissolved. The pale blue color of the solution produced is due to the copper in the coin. Sometimes little specks of black material are seen floating in the solution, and these may be finely divided gold, it being almost impossible to separate the last traces of this metal from silver on the commercial scale.

Silver chloride, AgCl, *silver bromide*, AgBr, *silver iodide*, AgI, are all formed as curdy precipitates when a solution of silver nitrate is treated with a solution of a chloride, a bromide, or an iodide. These compounds, which are insoluble in water, are all very sensitive to light, suffering some decomposition which is not very well understood.

EXPERIMENT.—Place a little of the solution of silver nitrate obtained in the last experiment in each of three test-tubes; to the first add a few drops of potassium (or sodium) chloride solution; to the second, potassium bromide; and to the third, potassium iodide. Expose part of each precipitate to the sunlight or to diffused daylight. To the other part of each add a strong solution of sodium thiosulphate.

Photography.—The art of photography is based mainly on the sensitiveness to light of the three compounds of silver just mentioned, the bromide being the one most frequently employed. A glass plate, or a celluloid film, is coated with a layer of gelatine containing silver bromide, all the work being done in the dark or in a very weak red light. The image formed by the lens of the camera is then allowed to fall on the silver bromide, generally only for a fraction of a second. Exactly what happens to the bromide is unknown, but when the developer—*i.e.*, a solution capable of extracting bromine—is subsequently poured over the plate, the silver bromide is reduced to finely divided metallic silver (*i.e.*, gives up its bromine) fastest where it was most highly illuminated, and with less speed where the illumination was less. When the reduction (development) has gone sufficiently far, the plate is washed and fixed, *i.e.*, immersed in a solution of sodium thiosulphate ("hyposulphite of soda," "hypo") which dissolves away what unchanged bromide of silver is left, but does not attack the metallic silver. The result is a negative, *i.e.*, a picture in which the original bright parts are dark, and *vice versa*. To obtain a print from this, a similar gelatine bromide emulsion (generally supported on paper) is pressed against the negative and light allowed to shine on to it through the latter; when this is developed and fixed, we have a negative of the negative, *i.e.*, a positive. Of course most of the processes mentioned above must be carried on in the dark or in very weak red light which has almost no effect on silver bromide.

The reaction between silver bromide and sodium thiosulphate is

$$2Na_2S_2O_3 + AgBr = Na_3Ag(S_2O_3)_2 + NaBr,$$

both the resulting compounds being soluble in water.

Copper.—In Roscoe and Schorlemmer's "Treatise on Chemistry," we read: "Copper of all the metals is the one which was first employed by man. This is explained by the fact that copper occurs in the native condition, and thus requires no metallurgical treatment. Copper was considered to be the metal specially sacred to Venus and in the writings of the alchemists is generally known by the name of this goddess."

Copper is found in nature both free and in combination. Native copper occurs in enormous masses near Lake Superior, and also in other localities; and other ores of copper, such as chalcocite, Cu_2S, and chalcopyrite, $CuFeS_2$, occur in many places.

There are a great many complicated processes of copper smelting, only one of which will be outlined here. Ores containing sulphur and iron are charged, with fuel and flux, into a special blast furnace, the products of which are slag and matte, which latter is a compound of copper, iron and sulphur. This matte is then run into a special form of bessemer converter; the air oxidises the sulphur to sulphur dioxide which passes off, the iron to ferrous oxide which combines with silica from the lining of the converter to form an easily fusible slag of iron silicate, and metallic copper is left. This copper is quite impure and is nowadays generally refined by an electrolytic process. The impure copper is cast into slabs which are hung in a bath of copper sulphate solution and connected to the positive pole of a battery (dynamo), while thin plates of pure copper connected to the negative pole are hung in the same bath. The process is one of copper-plating, pure copper being plated on to the pure copper plates while the copper of the impure slabs dissolves at the same rate. The impurities do not dissolve, but fall to the bottom of the bath as a slime which is afterwards worked up for the gold and silver which it contains.

Copper is a metal of a striking red color, having a density of about 9 and being an excellent conductor of heat and electricity. Its power of conducting is very much diminished by the presence of very small quantities of impurities, hence the need for a very perfect process of refining such as the electrolytic method just described. In dry air, copper is unattacked, but moist air slowly converts the surface into a greenish substance (a basic carbonate; verdigris is a basic acetate). It is easily dissolved by nitric acid, even when dilute; but most other dilute acids have little or no effect on it, unless air is present. It is important to remember this, because copper is used so much for cooking utensils. Food may contain small quantities of organic acids, but these will do copper vessels no harm if cooking be carried on with the lids on, because then the air is displaced by the steam. If, however, the cooking be carried on in open copper vessels, there is great likelihood of the metal being attacked.

The hydrogen of the acid does not seem to like to give up its hold on the rest of the acid unless it can get something in exchange. If oxygen be present, the hydrogen can then combine with it to form water, and is not left alone in the free state.

Copper is used a great deal in the construction of electrical apparatus, for roofing and for sheathing ships. In the form of alloys it is used for many other purposes. The most important of these alloys are given below, with their average compositions. It must be remembered that many of them vary very much according to the ideas of those who make them.

Bronzes—Coins	95% copper,	4% tin, 1% zinc
Medals	93% copper,	7% tin
Gun metal	90% copper,	10% tin
Bell metal	75% copper,	25% tin
Brass	66% copper,	34% zinc (very variable)
German silver	50% copper,	25% zinc, 25% nickel
Nickel coins	75% copper,	25% nickel
British gold coins	8.3% copper,	91.7% gold
British sterling silver	7.5% copper,	92.5% silver

Copper forms two series of compounds, cuprous in which the atom has a valence of one, and cupric in which the atom has a valence of two; the latter are by far the more common.

Cupric sulphate, $CuSO_4.5H_2O$, blue vitriol, blue-stone, may be made by dissolving copper in hot sulphuric acid and is obtained as a by-product in many industrial processes. It is used in electroplating, *i.e.*, covering surfaces with a layer of copper by means of the electric current, and in solution as the liquid in many batteries.

If a solution of some copper salt such as the sulphate be prepared and a piece of iron dipped into it, the iron becomes plated with copper, the following reaction taking place:

$$CuSO_4 + Fe = FeSO_4 + Cu$$

If the iron were left in the solution long enough it would be completely replaced by copper, and when this takes place extremely slowly (*i.e.*, when the copper solution is extremely dilute) the resulting copper retains the form of the original object and is quite hard. Iron tools left for years in copper mines where the mine waters contain a little copper sulphate in solution have thus been turned into copper tools. These changes were eagerly studied by the alchemists who believed that iron had actually been converted, transmuted, into copper; and if this were the case, why should not lead be turned into gold? It was Robert Boyle, about 1675, who proved that the copper existed in the solution first and that it and the iron merely changed places.

Copper chloride tinges the non-luminous flame a fine blue; most other copper compounds tinge the flame green.

Mercury.—This metal does not seem to have been known to the ancients, but is mentioned by Theophrastus, a Greek writer, about the year 300 B.C. It was of extreme interest to the alchemists who had strange ideas about its being one of the constituents of all other metals, and during the medical-chemical (iatro-chemical) period it and its compounds were much studied and used as medicines. It is often called quicksilver on account of the mobility of its drops (quick means alive—*cf.* "the quick and the dead"). Its Latin name, *hydrargyrum*, means water-silver.

It occurs both native and as the sulphide, HgS, cinnabar.

Mercury is silvery white in color and is the only metal that is liquid at ordinary temperatures; it freezes at −39.5° and boils at 357°. It is about 13.5 times as heavy as water. It alloys with a great many of the metals, and alloys containing mercury are called amalgams; some of these are solid and some liquid.

Certain amalgams seem to be definite chemical compounds, but most of them, like most alloys, are probably solutions (thus brass is a solid solution of copper and zinc).

Copper amalgams become quite plastic when warmed and do not harden again for several hours after cooling; on this account they are often used for filling teeth.

Mercury is used to a very great extent in physical and chemical apparatus such as barometers, thermometers, temporary electrical connections, etc. For these and other purposes it is generally purified by distillation.

It is unaffected by air and water at ordinary temperatures and behaves towards acids much as copper does; dilute acids, with the exception of nitric, do not attack it. It forms two oxides and two series of salts, the mercurous in which the atom has a valence of one, and the mercuric in which the atom has a valence of two.

Mercuric oxide, HgO, red precipitate, which played such an important part in the history of chemistry, may be prepared by heating mercury in the air for a long time to a temperature just below its boiling point. When the oxide itself is heated to a somewhat higher temperature it is decomposed, as we have already seen.

Mercuric chloride, $HgCl_2$, corrosive sublimate, is a white crystalline solid which is soluble in water. It is extremely poisonous but forms an insoluble compound with albumen. Hence, when it has been taken internally, white of egg should be given at once in large quantity. Corrosive sublimate, in dilute solution, is much used in surgery as an antiseptic, *i.e.*, to destroy disease-producing bacteria (low forms of living things).

Mercurous chloride, HgCl, calomel, is a white solid, insoluble in water. It is not poisonous and is used considerably in medicine.

Calomel is slowly decomposed by light, thus:

$$2HgCl = Hg + HgCl_2,$$

and the corrosive sublimate produced is a violent poison, as has already been mentioned. Hence, great care should be taken that calomel that is to be administered as a medicine should be protected from the light, and it should not be too old. Very serious cases of poisoning have resulted from disregarding these facts.

QUESTIONS

1. It is stated that silver has been known from earliest times: why do you think this was the case? Can you imagine any reason why metallic sodium has not been known as long—its compounds are much more abundant than those of silver?

2. From the ores of what other metals is silver often obtained as a by-product? Would you consider it a valuable by-product?

3. Why do silver coins become black when carried in the same pocket as ordinary matches? Why are silver spoons blackened by eggs? Ordinary rubber bands blacken silver: what element in their composition would this suggest?

4. Nitric acid is used in medicine as a cautery and so is silver nitrate—why are their actions somewhat similar?

5. What is the cause of the black stain produced by a solution of silver nitrate (marking ink) when placed on cotton?

6. Why do you think silver bromide is used in photography?

7. Photographically speaking, what is a developer, a fixer?

8. Give an outline of the process of making a photographic negative, telling, as far as possible, what chemical reactions take place.

9. What do you think would happen to a negative if the fixing were omitted?

10. Give an outline of a method of copper smelting.

11. What is copper matte, and what is meant by "bessemerising copper matte"?

12. Why do bronze statues turn a more or less greenish color as time goes on?

13. After the electrolytic purification of copper, gold and silver are found in the slimes obtained. Do you think that copper has been transmuted into these metals? If not, where did they come from?

14. Does the composition of various samples of brass be[illegible] the law of definite proportions? Do we, then, assume that brass is a compound? Do we assume that the law is useless?

15. Mention some of the important alloys of copper, with their quantitative compositions.

16. Write the formulas of cuprous and cupric oxides, and cuprous and cupric chlorides.

17. Is ordinary copper sulphate a cuprous or cupric compound? Why?

18. How do you explain what was formerly thought to be the transmutation of iron into copper?

19. If a bunsen burner becomes very dirty, the flame sometimes exhibits blue or green streaks. How do you account for this?

20. Why did the earlier chemists somewhat doubt the metallic character of mercury?

21. What are amalgams? Are they alloys?

22. Write the formulas of mercurous and mercuric oxides, and mercurous and mercuric nitrates.

23. Contrast calomel and corrosive sublimate as to (*a*) formula, (*b*) solubility, (*c*) poisonousness.

24. Explain why the use of old calomel as a medicine is risky.

25. What is there to recommend the use of silver for telegraph wires? What is there against it?

CHAPTER XXII

ZINC. ALUMINIUM. TIN. LEAD

With the exception of tin and lead, these metals are not specially related to one another. None of them are found native to any important extent (aluminium never, and zinc very doubtfully), but they are all very useful both in the metallic state and in the form of compounds. Zinc has a valence of two, aluminium of three, and tin and lead of two and four each.

Zinc was not recognised as a metal by itself until about 1700 A.D., although brass, obtained by smelting mixed ores of copper and zinc, had been known certainly as far back as the time of Aristotle. Zinc seems to have been prepared on the large scale first in England, about 1743.

In many respects zinc resembles magnesium. Thus, it is a dyad, its principal occurrence is as the carbonate, $ZnCO_3$ (calamine, smithsonite, or zinc spar); it also occurs largely as sulphide (ZnS, zinc blende) as so many of the metals do.

The ores are first roasted, *i.e.*, heated with free access of air, whereby the zinc compounds are converted into the oxide, ZnO, and then this is very highly heated with coal dust in a sort of fire-clay retort. when the zinc distils over and is condensed.

The metal is whitish with a bluish tinge, crystalline and somewhat hard and brittle. Its density is about 7 and it is soluble in most acids.

Between 100° and 150° it can be rolled into plates or drawn into wire, but at 205° it is so brittle that it can be powdered in a mortar.

Zinc is hardly affected at all by air and water; hence, it is used in the form of sheets for lining vessels intended to hold water, and as a thin film on iron, obtained by dipping the cleaned iron into melted zinc, to protect the iron from rusting. Such zinc-covered iron is called galvanised iron. Zinc is employed in the form of rods and plates in batteries. It is also used in many alloys such as brass, German silver, etc., which have already been mentioned.

Zinc oxide, ZnO, generally made by burning the metal, is used as a pigment under the name of zinc white, or Chinese white. It is not discolored by sulphur compounds, as white lead is, because zinc sulphide is white.

Zinc hydroxide, $Zn(OH)_2$, or H_2ZnO_2, acts as a base towards acids:

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O,$$

but as an acid towards strong bases:

$$2NaOH + H_2ZnO_2 = Na_2ZnO_2 + 2H_2O$$

Hence, zinc is both a base-forming and an acid-forming element; but it is more of the former than the latter.

Cadmium is a metal which is very similar in its properties and compounds to zinc, with which it is almost always associated in nature.

Aluminium.—It was long recognised that alum, clay and certain other substances must contain an undiscovered metal, but it was not till 1827 that it was prepared by Wöhler.

Aluminium is found in enormous quantities in nature, but always in combination. It occurs as the oxide (corundum) as a form of the hydroxide, $Al_2O(OH)_4$ (bauxite), in a large number of silicates such as orthoclase, $KAlSi_3O_5$ and in clay, $Al_2Si_2O_7.2H_2O$.

It is prepared from bauxite, $Al_2O(OH)_4$, by an electrical process.

Aluminium is tin-white in color and very light for a metal, its density being only 2.6. Only iron and copper exceed it in hardness and strength. It can be rolled into sheets and drawn into wire, but it is very difficult to work in the lathe because it sticks to the tools. No satisfactory method of soldering it is known. It is a good conductor of electricity (weight for weight, better than copper, though in wires of the same diameter, copper is superior). It tarnishes only slightly in air, and pure water has no effect on it; but water containing salts in solution corrodes it rapidly. Aluminium has a valence of three.

On account of its lightness and strength, it finds many uses in the construction of comparatively small apparatus. It is not very suitable for cooking utensils on account of the action of salt solutions on it and the difficulty of making repairs.

At high temperatures, aluminium has an intense affinity for oxygen, *i.e.*, is a very powerful reducing agent. A mixture of finely divided aluminium with iron oxide, called thermite, when ignited, undergoes a change which is approximately

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe$$

and the reaction is so energetic that a temperature of something like 3,000° is attained, the alumina, which is generally considered infusible, flowing like water. The tremendously high temperature of the products is made use of in welding steel rails, repairing broken iron shafts, castings, etc. By replacing the iron oxide in the mixture with other oxides, difficultly reducible metals, such as chromium, are easily obtained.

Aluminium oxide, Al_2O_3, alumina.—This occurs in nature as the mineral corundum. Transparent, colored varieties are ruby and sapphire, a common variety is emery, and alundum is an artificially prepared form. The compound is very hard and is therefore largely used as an abrasive, *i.e.*, for grinding and polishing.

Aluminium sulphate, $Al_2(SO_4)_3$, is prepared by treating bauxite or pure china clay with sulphuric acid (the process is somewhat complicated). It combines with many other sulphates to form alums. The best known of these is ordinary alum, $KAl(SO_4)_2 \cdot 12H_2O$.

Alum is used as a substitute for an acid in some baking powders because its carbonate reacts with water (is hydrolysed) giving the hydroxide and carbonic acid:

$$2KAl(SO_4)_2 + 6NaHCO_3 = 3Na_2SO_4 + K_2SO_4 + 2Al(HCO_3)_3$$
$$2Al(HCO_3)_3 + 6H_2O = 2Al(OH)_3 + 6H_2CO_3$$
$$H_2CO_3 = H_2O + CO_2$$

Aluminium silicates.—As already mentioned, clay is a silicate of aluminium, and felspar, mica, garnet and many other minerals are double silicates of aluminium and other metals.

On account of their plasticity when moist and their conversion into a hard, stone-like substance, unaffected by water, when highly heated, clays of various kinds are used in what are known as the *ceramic industries, i.e.*, the manufacture of bricks, tiles, pottery and porcelain. These products are made by mixing suitable clays while moist with proper proportions of other materials, such as sand, burned clay, etc., moulding the articles, drying them and then burning them. Glazing is effected by covering the surface with some suitable fusible mixture, either before the first baking or afterwards, and then baking again. Various decorations can be painted on with suitable pigments and then burned in by a subsequent firing.

Tin.—Up to about the year 700 there seems to have been a good deal of confusion between the metals tin and lead, many of the alchemists regarding them simply as differently colored varieties of one and the same metal (they called them *plumbum candidum* and *plumbum nigrum*). Tin was often called Hermes by the early Greek alchemists, but later it was called Zeus or Jupiter.

The most important ore of tin is the dioxide, SnO_2, called cassiterite by the mineralogists.

The principal process in the smelting of tin from this ore consists in heating it with powdered anthracite (carbon) when the following reaction takes place :

$$SnO_2 + 2C = Sn + 2CO$$

Of course ores are never pure, hence small quantities of metals other than the one sought are smelted too ; and, on this account, the first product obtained must generally be refined or purified. This is the case with tin, but we need not give the details of how this is done.

Tin is a white lustrous metal somewhat harder than lead; it can be easily rolled into thin sheets called tin foil. It is unaffected by dry or moist air or by water; hence it is often used for covering iron, copper, or brass by dipping articles made of these metals, and which have been carefully cleaned, into melted tin. The so-called "tin" of which tin plate, tin cans, etc., are made, is sheet iron or steel tinned in the way just described. Tin is also used in making many alloys, such as bronze, which is an alloy of tin and copper, and soft solder and pewter, which are alloys of tin and lead. Bearing, or anti-friction, metals are mainly alloys of antimony, tin and copper; their composition varies enormously, but antimony 10%, tin 85%, copper 5%, may be regarded as a sort of average. (Other metals such as zinc and iron are introduced into the cheaper or harder grades.)

Lead is mentioned in the book of Job and also in Numbers. As has already been said, tin and lead were not distinguished for many centuries, and even then, for a long time, were considered to be different varieties of the same metal. By the alchemists, "dull, heavy lead was apportioned to Saturn."

The most important ore of lead is the sulphide, galena, PbS, which is found in a great many parts of the world; it almost invariably contains some silver and occasionally a little gold.

The smelting of lead is a complicated process and will not be described in detail; this much may be said, however: lead sulphide is roasted in a current of air, whereby some of it is converted into oxide and some into sulphate, part of the sulphur going off as the dioxide, thus:

$$PbS + 3O = PbO + SO_2$$
$$PbS + 4O = PbSO_4$$

Then a reaction takes place between these oxidised products and more of the lead sulphide, whereby all the rest of the sulphur goes off as the dioxide and the lead is liberated :

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2$$

The lead thus obtained must be refined, but this process does not remove the silver and gold. To extract these two metals, some zinc is added to the melted lead (about 2%) and after thorough stirring the whole is allowed to stand quietly ; the zinc rises to the surface, just as oil would on water, and brings practically all the gold and silver with it ; this alloy is then skimmed off and subjected to distillation, the zinc going off and the gold and silver remaining behind.

Lead is a white metal with a bluish-gray tint ; it is soft enough to be easily cut with a knife and to leave a mark when drawn across paper, but is fairly tough ; it can be rolled into sheets but cannot be drawn into fine wire. It has a density of about 11.3. Freshly cut surfaces are bright, but they soon become dull and darker in color owing to superficial oxidation caused by the air. Pure water acting on clean lead produces $Pb(OH)_2$ which is slightly soluble, but ordinary water which contains carbonic acid produces a film of basic carbonate which is insoluble and protects the lead from further action. Water from swampy ground often contains traces of organic acids and these may dissolve some of the lead. As lead compounds are very poisonous, these facts should be kept in mind on account of the common use of lead pipes for water service. Lead is almost unacted on by sulphuric and hydrochloric acids ; other acids attack it rather easily.

Lead is used very largely for water pipes and in sheets for lining sulphuric acid chambers ; it is also employed to a large extent in storage batteries. Lead containing a little arsenic is used in making shot, and an alloy of lead, antimony and tin is type metal. Solder, lead and tin, has already been mentioned.

Lead forms several oxides (one of which is red lead) and a number of other compounds that are of importance in the arts; but only two of these latter need be mentioned here.

Lead acetate, $Pb(C_2H_3O_2)_2$, sugar of lead, is made by acting on lead with acetic acid. It is soluble in water and the solution has a sweet taste; it is used in medicine for reducing swellings, etc.

Basic lead carbonate, $2PbCO_3.Pb(OH)_2$, white lead.—This is one of the most important of all pigments, and is made by several processes, the old Dutch process being still the principal one employed. Earthenware pots, glazed inside, about eight inches deep and five inches high, and with a little shelf about a quarter of the way up, are used. Dilute acetic acid (often vinegar) is put in the bottom, and on the shelf is placed a spiral, or "buckle," made by rolling up a strip of sheet lead. A number of these pots are then placed on a layer of tan-bark and manure in a brick building, boards are placed on them and on top of this another layer of tan-bark and manure and then more pots and so on until the building is full. "For a stack 20 by 12 by 18 feet in size, 40 or 50 tons of lead are required, about 3 tons of lead and 200 gallons of acid being used in each layer of pots."—(Thorp). The stack is allowed to stand for two or three months. The vapors of acetic acid and water attack some of the lead, forming basic lead acetate, and then the carbon dioxide produced by the fermentation (rotting) of the tan-bark and manure, reacts with this, converting it into basic lead carbonate and acetic acid, which latter attacks more of the lead, and so the action goes on until all the lead is "corroded."

The reactions which appear to be rather complex are about as follows:—

$$Pb + 2HC_2H_3O_2 = H_2 + Pb(C_2H_3O_2)_2$$

$$3Pb(C_2H_3O_2)_2 + 2H_2O = 2Pb(C_2H_3O_2)_2.Pb(OH)_2 + 2HC_2H_3O_2$$

$$2Pb(C_2H_3O_2)._2Pb(OH)_2 + 2CO_2 + 2H_2O = 2PbCO_3.Pb(OH)_2 + 4HC_2H_3O_2$$

The white lead formed in this way is carefully separated from any unaltered metallic lead and is then finely ground. It is the most important of all white pigments, but is liable to darken in time on account of the trace of sulphur compounds in the air which form black lead sulphide, PbS. It may often be bleached again by the action of hydrogen peroxide which converts the black PbS into white $PbSO_4$.

Titanium, Zirconium, Cerium, Thorium are related to tin and lead. The last two are of interest because Auer light mantles (invented by the Austrian professor, Dr. Auer von Welsbach) consist of the oxides of these two metals, CeO_2, ceria, and ThO_2, thoria, mixed in the proportion of 1% of the former to 99% of the latter. Curiously enough, no other proportions give anything like as good a result. The reason for this is at present entirely unknown.

QUESTIONS

1. What is the higher valence of tin and lead? What non-metallic elements exhibit this valence? Write the formulas of the higher oxides of these four elements.

2. In what way does zinc resemble magnesium?

3. Write the equation representing the reaction that takes place when zinc sulphide is roasted.

4. Do you think that molten zinc can be made to boil? Why?

5. Mention some uses of zinc.

6. Why is zinc white not discolored by sulphur compounds?

7. Are the metals elements or compounds? How about brass?

8. By consulting the text, tabulate the ordinary metals in order of their densities, and write in the densities. (By means of this table try to remember the relative densities in a general way.)

9. What, chemically, are ruby, diamond, sapphire, carnelian?

10. Mention some things that you have seen that are made of aluminium. What is there for and against its use for cooking utensils?

11. What is thermite, and for what is it used? (A great deal was used by the Russian fleet during the Russo-Japanese war.)

12. What are emery and alundum, and for what are they used?

13. What is the composition of ordinary baking powders? Why is it possible to use alum as a substitute for one of the constituents in such powders?

14. What are the ceramic industries? What is the principal raw material used in them? Why?

15. Read the article on pottery in some good encyclopædia, make an abstract of it, and then tell some one about it.

16. What observation made almost every day would lead you to think that tin is malleable?

17. What is the "tin" of which tin cans are made?

18. Mention some important alloys of tin, and state what other metals they contain and what they are used for.

19. By what steps are the lead and sulphur of galena separated?

20. How are gold and silver separated from lead?

21. Packages of chocolates and cigarettes, and packages of tea, are often wrapped in metal foil, but the foil looks very different in the two cases. What do you think it is in each case?

22. What properties of lead should be kept in mind when selecting pipes for water service?

23. Write the equation representing the dissolving of lead in acetic acid. Would lead taps be good on vinegar barrels?

24. What white pigment would you choose for use in a chemical laboratory, and why?

25. Tell what you know about Auer light mantles.

CHAPTER XXIII

GOLD. PLATINUM

These two metals are found almost exclusively in the native state, and are used mainly in the metallic condition. They form compounds (oxides and salts), but these are not of prime importance.

Gold.—On account of its occurrence in the native state in a great many parts of the world, its brilliant yellow color and the ease with which it is worked, gold was probably the first of all metallic substances to attract the attention of man. It is mentioned in the Old Testament and in Homer, and there are pictures on ancient Egyptian tombs showing men engaged in melting and weighing it. The alchemists called it Sol, the sun, the greatest and most perfect of all the metals; it was also called *rex*, the king of metals. For centuries the most laborious and persistent efforts were made to discover some method of transmuting the base metals into the noble metal, gold, not only on account of its money value but because it was supposed to possess marvellous properties, medicinal and otherwise.

Gold occurs almost always in the native state, containing more or less silver—sometimes enough to make it quite pale in color. Compounds of gold are very rare. Native gold occurs either *in situ*, in quartz veins, or reefs, and other rocks; or it is found in the sands, gravels and clays formed by the disintegration of these rocks and transported by rivers and streams to the places where we now find them deposited.

Such alluvial gold-bearing deposits are called *placers*. When in reefs, the rock is mined and then pulverised by means of stamp mills and the whole, mixed with water, run over amalgamated copper plates, *i.e.*, copper plates the surface of which has been coated with mercury. The gold sticks to and partially dissolves in the mercury, while everything else is carried on by the water. From time to time the gold amalgam is scraped off the plates, the mercury distilled off, and the residual gold melted down and refined. In the case of placer gold, the gold and gravel, sand, or clay, are separated by currents of water in suitable apparatus ("washing"), the lighter worthless material being washed away and the heavier gold caught in suitable grooves.

Of late years a process known as *cyaniding* has been introduced and is worked on an enormous scale in the case of low grade ores. Gold is attacked by a weak solution of potassium cyanide in presence of air according to the following equation:

$$2Au + 4KCN + O + H_2O = 2KAu(CN)_2 + 2KOH$$

The potassium auricyanide produced is soluble in the water present and is thus separated from the rest of the rock. The gold is separated from the solution thus obtained either by precipitation by metallic zinc (much as copper is precipitated from its solutions by metallic iron) or by an electrical process.

Gold obtained by the methods mentioned above always contains silver and generally other metals and must therefore be refined. There are several methods for doing this.

Gold exhibits a bright yellow color by reflected light, quite unlike that of any other metal; by transmitted light, *i.e.*, when thin films are looked through, it is green. Its density is 19.3. It is the most malleable and ductile of all the metals. To give some idea of the extent to which these processes may be carried, the following figures are quoted: 100 square feet of gold leaf weigh one ounce and the leaves are so thin that 280,000 of them, placed one on the other, would measure one inch in thickness. Two miles of fine silver wire can be gilt with one grain of gold and the thickness of the deposit is about 0.000,002 mm. (Such wire is used in the manufacture of gold lace.) Gold is extremely ductile and wire can be drawn so fine that 3,400 metres weigh only one gram.

Pure gold is very soft and articles made of it wear away fast if used; hence, to make it harder for use in coinage and jewellery, it is alloyed with copper, or silver, or both; copper makes it reddish, silver makes it pale, while the two in proper proportions change its color only very little. The fineness of gold is generally expressed in carats, 24 carats being pure. English gold coins are 22-carat fine, *i.e.*, $\frac{22}{24}$ of the coin is gold, while gold chains, etc., are generally 18-carat.

The word gold is supposed to be derived from an old root that means to glitter. It is well to remember, however, that "all is not gold that glitters." Ignorant people are continually imagining that they have discovered gold in rock or sand because they have found something that is yellow and shiny. If they would remember that, when tried with a penknife, gold cuts like lead, while these other yellow minerals either are too hard to be marked with the knife (pyrite) or else cut to a powder, as slate would (copper pyrites, yellow mica, etc.), they would be saved from much disappointment.

Gold is not affected by oxygen at any temperature, or by water, or by sulphur, or by any single acid (except the very rare acid, selenic). Hence, it is a "noble" metal in the extreme sense of the term. It is, however, attacked by chlorine, and therefore by *aqua regia*, a mixture of hydrochloric and nitric acids, soluble auric chloride, $AuCl_3$, being formed.

Platinum.—This metal is found free in nature, but nothing much was known about it till about 1750, when it was discovered by the Spaniards in America. The name comes from the Spanish *platina*, the diminutive of *plata*, silver. The most important deposits known are in the Ural mountains. (Small quantities have been found in British Columbia.)

Platinum is grayish-white in color, fairly hard, and has a density of 21.5—about the heaviest substance known. It is very malleable and ductile and melts at about 1775°, and hence is infusible in all ordinary flames and furnaces, but can be melted fairly easily in the flame of the oxy-hydrogen blowpipe and in the electric arc. At a red heat it is easily welded. It is a good conductor of heat and electricity. It is unaffected by air or water at any temperature and is unattacked by any single acid, just as gold is, but *aqua regia* converts it into soluble plantinic chloride, $PtCl_4$. It is somewhat attacked by fused alkalies.

Platinum is a very valuable catalytic agent in a large number of chemical reactions, especially when in a fine state of division (*e.g.*, contact method for the **manufacture of sulphuric acid**). This action seems to be connected with the **power it possesses of absorbing gases. Palladium,** a metal closely allied to **platinum, is capable of absorbing** 900 times its own volume of hydrogen under **certain conditions.**

Platinum, in spite of the fact that it costs more than gold, is used in the making of chemical apparatus that must resist high temperatures and the action of strong acids; it is used in stills for evaporating sulphuric acid, for crucibles, dishes, forceps, spatulas, electrodes, etc., in the laboratory, and for that portion of the wire in incandescent electric light bulbs that is sealed through the glass—the portion inside the bulb is carbon, or tungsten, the latter a rare metal which is also called wolfram.

Iridium occurs with platinum and resembles it somewhat in properties, but is very much harder. It is often alloyed with platinum to increase the hardness of the latter. This alloy is frequently used for pointing gold pens.

QUESTIONS

1. Why has gold attracted the attention of man as it has done?

2. How is gold obtained from gold quartz?

3. What property of gold is made use of in "washing" gold-bearing sands and gravels?

4. What is meant by "cyaniding"? Describe the process.

5. Gold letters on shop windows look yellow when looked *at*, but green when looked *through*. What statements in the text are in accordance with these facts?

6. How might the gold and silver in an alloy of these two metals be separated?

7. What percentage of pure gold is there in a 20-carat wedding ring, and in an 18 carat watch chain?

8. Describe a simple test to determine whether yellow particles found in a rock are gold or not. [illegible] brass is not brittle lessen the value of this test?

9. How could you distinguish a brass "gold brick" from a lump of genuine gold?

10. Why [illegible]?

11. How [illegible] capable of dissolving gold?

12. How could you distinguish [illegible] real gold?

13. About how [illegible] that would fill an ordinary [illegible]?

14. Would th[illegible] or base metal, had [illegible] Why?

15. Would [illegible] chemically active or inactive? Why?

16. What [illegible] as a metal for coinage? Would calcium [illegible] as good [illegible]?

17. How may [illegible] be distinguished from silver?

18. [illegible] does its action as a catalyst seem [illegible] that exhibits this property to an extraordinary degree.

19. Why [illegible] platinum [illegible] in the making of chemical apparatus? [illegible] ordinary cooking utensils?

[illegible] you [illegible] reason why so few experiments are given [illegible] these metals? (Is there a blast-furnace in your [illegible]

[illegible] ways in which chemistry has been of use (*a*) to [illegible], (*c*) to the business man.

[illegible] sit at home, and notice how many objects there [illegible]ry of which you know something.

23. What do you think of regarding earth, air, fire, and water, as the four fundamental substances or elements? Would you blame a young child because he did not know all of chemistry?

24. Are we to consider that all the chemical views held at the present time are correct? Why, then, should we hold them at all? Is your penknife perfect? Why, then, not throw it away? How long do you intend to keep it? What is it, connected with your penknife, that makes you wish to keep it?

25. You will be told that *I* (some old man) got along very well without any knowledge of chemistry. Can you think of any other things he got along very well without, but which we like to have? Some folks do not use soap and cannot read. Are these people competent judges of the value of soap and of the ability to read?

INDEX

PAGE
Absolute scale of temperature 46
Absolute zero 46
Acetic acid 177
Acetylene 159, 165
Acetylene series 164
Acid 103, 107
Acid anhydrides 116
Acid-forming elements 97
Acid reaction 104
Acid salts 122
Acids, basicity of 122
Acids, dibasic 122
Acids, general method of preparing 91
Acids, monobasic 122
Acids, tetrabasic 122
Acids, tribasic 122
Action, chemical, classes of 25
After-damp 163
Agate 187
Air 126
Air, dephlogisticated 22
Air, inflammable 37
Air-slaked lime 209
Alabaster 109, 212
Albumins 182
Alchemistic period 15, 16
Alchemists 16
Alcohol, common 172
Alcohol, denatured 175
Alcohol, ethyl 172
Alcohol, wood 172
Alcohols 172
Alkaline earths 207
Alkaline earths, metals of the 207
Alkaline reaction 104
Alkalis 194
Alkalis, metals of the 194
Alkaloids 183
Allotropy 35
Alloys 233
Alumina 238

PAGE
Aluminium 237
Aluminium oxide 238
Aluminium silicates 239
Aluminium sulphate 238
Alums 238
Alundum 238
Amalgams 233
Amethyst 187, 188
Ammonia 131, 132
Ammonia-soda process 198
Ammonium 203
Ammonium chloride 203
Ammonium hydroxide 134, 203
Ammonium sulphate 204
Amorphous solids 111
Amorphous sulphur 112
Analysis 25
Ancient period 15
Anhydrides 116
Aniline 179
Animal charcoal 153
Anions 106
Anode 107
Anthracite 154
Antichlor 122
Antimony 148
Antiseptic 65
Apollinaris water 155
Aqua ammonia 133
Aqua fortis 134
Aqua regia 136, 247
Aqueous tension 48
Argentite 227
Argon 127, 130
Aristotle, elements of 55, 124
Aromatic compounds 178
Aromatic series 164
Arrhenius, Svante 108
Arsenic 148
Arsenious oxide 148
Arsenopyrite 148

PAGE
Arsine 118
Asbestus 217
Ashes, wood 200, 201
Assimilation of nitrogen 130
-ate, termination 96
Atmosphere 126
Atmospheric nitrogen 126, 127, 131
Atom 70, 71
Atomic ratio 78
Atomic theory 68, 70
Atomic weight 71
Atomic weights, determination of 73
Atomic weights of commoner elements 76
Atomic weights, table of 263
Auer-light mantles 170, 213
Auric chloride 247
Avogadro's hypothesis 51

Bacteria in water 61
Baking powders 199, 238
Baking soda 199
Baku, Holy Fire of 163
Ballard 98
Balloons 40
Barium 218
Base 104, 107
Base-forming elements 97, 191
Base metals 16, 190
Bases 103
Basic anhydrides 116
Basic reaction 104
Basicity of acids 122
Bauxite 237
Beans 182
Bearing metal 240
Beer 174
Bell metal 232
Bengal saltpeter 201
Benzene 179
Benzene series 164
Benzine 164
Benzol 179
Bessemer process 223
Biology 16
Bismuth 149
Bittern 92
Bituminous coal 154
Black, Joseph 127, 155
Black-ash 197

PAGE
Black lead 152
Blast furnace, copper 230
Blast furnace, iron 220
Blaugas 165
Bleaching 65, 115
Bleaching action of chlorine 88
Bleaching powder 90, 216
Blood 182
Blood-stone 187
Blue John 100
Blue-stone 232
Blue vitriol 232
Bog iron 220
Boiler-scale 214
Bone-black 153
Bones 216
Boracic acid 189
Borax 189, 199
Boric acid 189
Boron 189
Bort 151
Boyle, Robert 15, 142, 232
Boyle's Law 45
Brand 142
Brandy 175
Brass 232
Bread 181
Bricks 239
Brimstone 110
British gum 181
Bromides 99
Bromine 98
Bronzes 232
Bunsen, Robert 168
Bunsen burner 168
Burette 105
Butter-fat 183
Butyric acid 177
By-products 198

Cadmium 237
Caffein 184
Cairngorm 187
Calamine 236
Calcite 210
Calcium 207
Calcium bicarbonate 210
Calcium carbide 159, 216
Calcium carbonate 210
Calcium chloride 216

PAGE
Calcium hydroxide 209
Calcium light 41
Calcium oxide 207
Calcium phosphate 216
Calcium silicate 214
Calcium sulphate 212
Calculations 81
Calomel 234
Calx 18
Candle, burning of 18, 19, 20
Cane sugar 180
Cannizzaro 53
Caramel 180
Carat 247
Carbide 216
Carbides 159
Carbohydrates 179
Carbolic acid 179
Carbon 150
Carbon dioxide 154
Carbon disulphide 159
Carbon family 97
Carbon monoxide 158
Carbon tetrachloride 172
Carbonado 151
Carbonates 157
Carbonic acid 157
Carbonic acid gas 154
Carborundum 188
Carnallite 217
Carnelian 187
Caseïn 187
Cassiterite 239
Cast iron 222
Catalysers 28, 117
Catalysis 28
Caustic, lunar 228
Caustic potash 201
Caustic soda 195
Cavendish, Sir Henry 37
Celluloid 181
Cellulose 180
Cement, Portland 215
Cementation process 223
Ceramic industries 239
Ceresine 101
Ceria 243
Cerium 243
Chalcedony 187
Chalcocite 230

PAGE
Chalcopyrite 109, 230
Chalk 210
Chamber acid 119
Chamber process 118
Change, chemical 12
Change, physical 12
Charcoal 153
Charcoal, animal 153
Charles's Law 46, 47
Cheese 183
Chemical action, classes of 25
Chemical change 12
Chemical nitrogen 126, 127
Chemical nomenclature 96
Chemical properties 30
Chemical pulp 181
Chemical revolution 23, 124
Chemistry, definition of 12
Chemistry, history of 15
Chemistry, medical 17
Chili nitre 199
Chili saltpeter 199
Chinese white 237
Chloride of lime 90, 216
Chlorides 92
Chlorine 85
Chlorine, acids of 95
Chlorine, oxides of 95
Chlorine family 97, 98
Chloroform 172
Choke-damp 163
Cider 175
Cinnabar 233
Citric acid 178
Classification of elements 97
Clay 200, 239
Coal 150, 154
Coal gas 165
Cobalt 225
Cocaine 184
Coffee 184
Coins, copper 232
Coins, gold 247
Coins, nickel 225
Coins, silver 228
Coke 153, 165
Collecting gases, method of 27
Collodion 181
Combination, chemical 24
Combining proportions, Laws of 68

PAGE
Combustion 23, 155
Combustion, spontaneous 33
Combustion, study of 18
Compound 21
Compound radical 134
Compounds, classes of 103
Concentrated lye 195
Conservation of energy, Law of 20
Conservation of mass, Law of 20, 72
Conservation of matter, Law of 20
Contact process 120
Converter, Bessemer 223
Copper 230
Copper chloride 233
Copper pyrites 109
Copper sulphate 232
Copperas 225
Coral 210
Corrosive sublimate 231
Corundum 238
Cotton 180
Courtois 99
Cream of tartar 199
Crucible steel 224
Crystallisation 58
Crystallisation, water of 58
Crystallography 110
Crystals 58, 110
Cullinan diamond 152
Cupric compounds 232
Cuprous compounds 232
Cyaniding of gold ores 246
Cyanogen 164

Dalton, John 70
Davy, Sir Humphrey 85, 171, 194, 207
Davy lamp 171
Deacon's process 90
Decay 33, 155
Decay of organic matter 131
Decrepitation 196
Definite proportions, Law of 68
Deliquescent substances 59
Denatured alcohol 175
Densities of gases 52
Dephlogisticated air 22
Dephlogisticated marine acid air 85
Derbyshire spar 100
Destructive distillation 131, 177
Development, photographic 229

PAGE
Dextrin 181
Dextrose 179
Diad 95
Diamond 151
Dibasic acids 122
Diffusion of gases 48
Disinfecting 115
Displacement, downward 87, 155
Displacement, upward 132, 155
Distillation 57
Distillation, destructive 131, 177
Distillation, fractional 173
Distilled liquors 175
Distilled water 61
Dolomite 217
Double decomposition 105
Downward displacement 87, 155
Drummond light 41
Dynamite 176

Earths 207
Earths, alkaline 207
Earth's crust, composition of 26
Eau de Javelle 199
Efflorescent substances 59
Egg 182
Electrodes 107
Electrolysis 107
Electrolytes 107
Electrolytic dissociation, theory of 106
Electrolytic refining of copper 230
Electroplating 108, 228, 232
Element 21
Elements, symbols of 263
Elements, table of 263
Elements of Aristotle 55
Elixir of life 16
Emery 238
Energy, conservation of 20
Enriched water-gas 165
Epsom salt 217
Equations 80
Equilibrium, chemical 116
Esters 177
Etching of glass 101
Ether, ethyl 176
Ether, sulphuric 176
Ethereal salts 177
Ethers 176
Ethyl alcohol 172

PAGE
Ethylene series ... 164
Eudiometer ... 60
Experiment ... 21
Explosions ... 41, 163

Families of elements ... 97
Fats ... 177
Fatty acids ... 176
Felspar ... 200
Fermentation ... 155, 172
Ferric compounds ... 225
Ferric hydroxide ... 225
Ferrous compounds ... 225
Ferrous sulphate ... 225
Ferrous sulphide ... 225
Fertilisers ... 147
Fibrin ... 182
Filter, chemical ... 29
Filtration ... 29, 56
Fire, as a test ... 17
Fire-damp ... 163
Fire extinguisher ... 157
Fixed air ... 127
Fixing of negatives ... 229
Flame ... 166
Flashing point ... 165
Flash-lights ... 217
Flint ... 187
Flour ... 182
Flowers of sulphur ... 110
Fluorine ... 98, 100
Fluor-spar ... 100
Food ... 183
Fool's gold ... 109, 220
Formaldehyde ... 172
Formalin ... 172
Formic acid ... 177
Formula ... 77
Formula, determination of ... 77
Formulas, graphic ... 95
Fractional distillation ... 173
French Revolution ... 196
Fusible metal ... 119

Galena ... 109, 240
Galvanised iron ... 237
Gas, coal ... 165
Gas Laws ... 44
Gas, natural ... 163
Gases, collecting ... 27

PAGE
Gases, densities of ... 52
Gases, diffusion of ... 48
Gases, solubility of ... 92, 156
Gases, volumes of ... 44
Gasoline ... 164
Gay-Lussac's Law ... 46, 47
Gay-Lussac tower ... 119
Geology ... 11
German silver ... 225, 232
Gin ... 175
Glass ... 214
Glauber, Johann Rudolf ... 91
Glauber's salt ... 199
Glover tower ... 119
Glucose ... 179
Gluten ... 182
Glycerine ... 175, 178
G. M. V. ... 52
Gold ... 245
Gold, amalgamation of ... 246
Gold chloride ... 247
Gold coins ... 232
Gold washing ... 246
Gradation (graduation) ... 196
Gram-molecular volume ... 52
Grape sugar ... 179
Graphic formulas ... 95
Graphite ... 152
Green vitriol ... 225
Gun-cotton ... 181
Gun-metal ... 232
Gunpowder ... 201
Gypsum ... 109, 212

Hæmatite ... 220, 225
Hair ... 183
Halogen derivatives of paraffins .. 171
Halogens ... 98
Hammer-scale ... 18, 21, 31, 225
Hard water ... 212
Hardening of steel ... 224
Hardness, permanent ... 213
Hardness, temporary ... 213
Hartshorn, spirits of ... 132
Heat of combustion ... 169
Helium ... 131
Hexad ... 95
Hexagonal system ... 111
History of chemistry ... 15
Holy Fire of Baku ... 163

PAGE

Homologous series 164
Horn 183
Hydraulic lime 210
Hydriodic acid 100
Hydro-, prefix 96
Hydrobromic acid 99
Hydrocarbons 163
Hydrochloric acid 91
Hydrocyanic acid 159
Hydrofluoric acid 101
Hydrogen 37
Hydrogen atom, weight of 73
Hydrogen dioxide 65
Hydrogen peroxide 65
Hydrolysis 217
Hydroquinone 179
Hydrosulphuric acid 112
Hydroxyl 104
Hydroxyl derivatives of paraffins 172
Hypo 122, 199, 229
Hypo-, prefix 96
Hyposulphurous acid 122
Hypothesis 49
Hypothesis, Avogadro's 51

Iatro-chemical period 15, 17
Iatro-chemistry 17
-ic, termination 96
Iceland spar 210
-ide, termination 96
Industrial alcohol 175
Inflammable air 37
Ink, marking 228
Ink, printer's 153
Ink, writing 225
Iodides 99
Iodine 98, 99
Iodoform 172
Ions 106
Iridium 218
Iron 220
Iron, galvanised 237
Iron oxides 225
Iron pyrites 109
Iron sulphide 71
Isomerism 179
Isometric system 110
-ite, termination 96

Jasper 187
Javelle water 199

PAGE

Kaolin 200
Kathode 107
Kations 106
Kelp 99
Kerosene 164
Kilns, continuous 208
Kilns, intermittent 208
Kindling point 32
Krypton 131

Lactic acid 178, 180
Lactose 180
Lamp-black 153
Laughing gas 138
Lavoisier, Antoine Laurent 22, 37, 151, 155
Lavoisier's experiment 23
Law, Boyle's 45
Law, natural 49
Law of Charles 46, 47
Law of conservation of energy 20
Law of conservation of mass 20, 72
Law of conservation of matter 20
Law of definite proportions 68
Law of Gay-Lussac 46, 47
Law of multiple proportions 69
Laws of combining proportions 68
Lead 240
Lead acetate 242
Lead, basic carbonate 242
Lead, black 152
Lead chambers 119
Lead oxides 242
Lead pencils 152
Leblanc, Nicholas 197
Leblanc soda process 197
Legumin 182
Life force 161
Lignite 154
Lime 207
Lime-kilns 208
Lime-light 41
Lime-water 209
Limestone 210
Limonite 220
Linen 180
Liquor ammoniae 133
Litmus 101
Lixiviation 198
Lodestone 225

PAGE
Lubricating oils 161
Luminosity in flames 167
Lunar caustic 228
Lye, concentrated 195

Magnesia 217
Magnesite 217
Magnesium 217
Magnesium carbonate 217
Magnesium chloride 217
Magnesium hydroxide 217
Magnesium nitride 217
Magnesium oxide 217
Magnesium silicates 217
Magnesium sulphate 217
Magnesium, burning of 18, 217
Magnetite 220, 225
Malic acid 178
Malt 174
Malting 181
Manganese dioxide 28, 34
Manure, barnyard 147
Marble 210
Marine acid air 91
Marking ink 228
Marsh gas 163
Mass, Law of conservation of 20, 72
Matches 141, 145
Mathematics 10
Matte, copper 230
Matter 11, 12
Matter, Law of conservation of 20
Mead 175
Meat 182
Mechanical pulp 181
Medical chemistry 17
Meerschaum 217
Mercuric chloride 234
Mercuric compounds 233
Mercuric oxide 234
Mercurous chloride 234
Mercurous compounds 233
Mercury 233
Metallic lustre 191
Metallic radical 203
Metallurgy 192
Metals 97, 190, 191
Metals, base 16
Metals, characteristics of 191
Metals, classification of 192

PAGE
Metals, noble 16
Metals of the alkaline earths 207
Metals of the alkalis 194
Metathesis 105
Meteorites 220
Methane 163
Method, scientific 53, 69
Methyl alcohol 172
Methylated spirits 175
Microcosmic salt 147
Milk 178, 182, 183
Milk, composition of 183
Milk of lime 209
Milk sugar 180
Mineral waters 63
Minerals 192
Mirrors 228
Mixtures 24
Modern period 15, 19
Moissan, Henri 100, 152
Molecular theory 44, 49
Molecular weights, determination of 51
Molecule 50
Monad 95
Monobasic acids 122
Monoclinic sulphur 111
Monoclinic system 111
Morphine 184
Mortar 210
Mother of vinegar 177
Multiple proportions, Law of 69
Muriatic acid 91
Myosin 182

Naphtha 164
Nascent state 89
Native 109, 192
Native metals 192
Natural gas 163
Natural law 49
Natural waters 62
Necrosis 143
Negative, photographic 229
Neon 131
Neutralisation 105, 106, 107
Newton, Sir Isaac 151
Nickel 225
Nickel coins 225, 232
Nicotine 184

PAGE
Nitrates 136
Nitre 201
Nitric acid 131, 134
Nitric anhydride 140
Nitric oxide 139
Nitrogen 124
Nitrogen, oxides of 137
Nitrogen family 97
Nitrogen peroxide 139
Nitro-glycerine 175
Nitrous acid 136
Nitrous anhydride 139
Nitrous oxide 138
Noble metals 16, 190
Nomenclature, chemical 96
Non-luminous flames 168
Non-metals 97
Normal pressure 14
Normal salts 122
Normal temperature 45

Oil gas 165
Oil of vitriol 118
Oils 177
Oleic acid 178
Olein 178
Olive oil 178
Onyx 187
Opal 187
Open-hearth process 223
Opium 181
Ores 192
Organic chemistry 161
Orpiment 148
Orthoclase felspar 200
Orthorhombic system 111
-ous, termination 96
Oxalic acid 178
Oxidation 32
Oxide 32
Oxidised silver 228
Oxidising agent 32
Oxygen 22, 26
Oxygen mixture 28
Oxy-hydrogen blowpipe 41
Ozone 31

Palladium 218
Palm oil 178
Palmitic acid 177

PAGE
Palmitin 178
Paper 180
Paraffin series 164
Paraffin wax 164
Paraffins 163
Paraffins, derivatives of 171
Paris green 148
Pearl ash 201
Peas 182
Peat 154
Pentad 95
Per-, prefix 96
Periodic classification 98
Permanent hardness 213
Peroxide of hydrogen 65
Perry 175
Petroleum 164
Pewter 210
Phenol 179
Philosopher's stone 16
Phlogistic period 15, 17, 19
Phlogiston 18
Phosphine 146
Phosphonium compounds 146
Phosphoretted hydrogen 146
Phosphoric acid 146
Phosphorite 142
Phosphorous acid 146
Phosphorous anhydride 146
Phosphorus 142
Phosphorus, red 144
Phosphorus, yellow 143
Phosphorus pentoxide 146
Phossy jaw 143
Photography 229
Physical change 12
Physical properties 30
Physics 12
Pig iron 222
Pine apple 177
Pintsch gas 165
Placers 246
Plaster of Paris 212
Plastic sulphur 112
Platinic chloride 218
Platinum 217
Plumbago 152
Pneumatic trough 27
Porcelain 239
Porter 174

PAGE
Portland cement 215
Positive, photographic 229
Potable water 63
Potash 200, 201
Potassium 200
Potassium bromide 201
Potassium carbonate 201
Potassium chlorate 201
Potassium chloride 201
Potassium cyanide 202
Potassium hydroxide 201
Potassium iodide 201
Potassium nitrate 201
Potassium sulphate 202
Pottery 239
Precipitate 92
Precipitate, red 22
Precipitation 92
Pressure, standard (normal) 44
Priestley, Joseph 22, 26, 91, 138
Print, photographic 229
Properties, physical and chemical. 30
Propionic acid 177
Proteids 182
Protoplasm 183
Prussic acid 159
Psychology 10
Puddling 222
Pulp, wood 180
Pyrite 109, 220
Pyrocatechin 179
Pyroligneous acid 172, 177

Quantitative period 15, 19
Quantivalence 94
Quartz 187
Quartzite 187
Quicklime 207
Quicksilver 233
Quinine 184

Radical, compound 134
Radical, metallic 203
Radio-active changes 70
Radium 70
Ramsay, Sir William 127
Rayleigh, Lord 127
Realgar 148
Red lead 242
Red phosphorus 144

PAGE
Red precipitate 22, 234
Reducing agent 41, 154
Reduction 41
Regular system 110
Rennet 183
Replacement 42
Resorcin 179
Respiration 23, 33, 155
Reverberatory furnace 222
Reversible reactions 116
Revolution, chemical 23, 124
Revolution, French 196
Rhigolene 164
Rhombic sulphur 111
Roasting 115
Rock crystal 187
Rock salt 195
Roll sulphur 110
Rose-quartz 187
Ruby 238
Rum 175
Rust 225
Rutherford 124, 127

Safety lamp 171
Safety matches 145
Sal-ammoniac 203
Saleratus 199
Sal-soda 198
Salt, common 195
Salt-cake 197
Saltpeter 201
Salts 106, 107
Salts, acid 122
Salts, naming of 96
Salts, normal 122
Sand 187
Sandstone 187
Sapphire 238
Scheele, Karl Wilhelm 85
Science 10
Science, applied 11
Science, mixed 11
Science, practical 11
Science, pure 11
Sciences 10
Scientific method 53, 69
Sea water 63
Selenium 122
Seltzer water 155

PAGE
Semi-metals 190
Series, homologous 161
Serpentine 217
Shellac 172
Shells 210
Shot 148, 211
Siderite 220
Siemens-Martin process 223
Silica 187
Silicates 188
Silicic acids 188
Silicon 187
Silicon carbide 188
Silicon dioxide 187
Silicon tetrafluoride 101
Silver 227
Silver bromide 228
Silver chloride 228
Silver coins 232
Silver iodide 228
Silver nitrate 228
Skin 183
Slag 221
Slaked lime 209
Slaking of lime 208
Slow oxidation 33
Smalt 225
Smithsonite 236
Smokeless powder 181
Smoky quartz 187
Soap 178
Soapstone 217
Sociology 10
Soda 196
Soda, caustic 195
Soda crystals 198
Soda water 157
Soda-ash 196
Sodium 194
Sodium bicarbonate 198, 199
Sodium carbonate 196
Sodium chlorate 200
Sodium chloride 195
Sodium hydroxide 195
Sodium hypochlorite 199
Sodium nitrate 199
Sodium oxides 194
Sodium peroxide 194
Sodium pyroborate 199
Sodium silicate 199

PAGE
Sodium sulphate 199
Sodium sulphite 199
Sodium thiosulphate 199
Softening of water 213
Solder 210
Solubility of gases 92, 156
Solutions 24
Solvay process 198
Solvent universal 16, 62
Sparklet bulbs 156
Spathic iron 220
Spectroscope 202
Specular iron 220
Spiegel iron 222
Spirit of salt 91
Spirits of hartshorn 132
Spirits of wine 172
Spontaneous combustion 83
Stalactites 211
Stalagmites 211
Standard pressure 44
Standard temperature 45
Starch 158, 181
Stassfurt 200
Stearic acid 177
Stearin 178
Steel 223
Sterling silver 228
Stibine 148
Stibnite 148
Stout 174
Stove-polish 152
Strontium 218
Strychnine 184
Study, value of 13
Sublimation 203
Substitution 42
Substitution products 171
Suet 177
Sugar, cane 180
Sugar, grape 179
Sugar, milk 180
Sugar of lead 212
Sulphates 121
Sulphides 114
Sulphites 116
Sulphur 109
Sulphur, native 109, 114
Sulphur dioxide 114
Sulphur family 97

PAGE
Sulphur flowers 110
Sulphur springs 112
Sulphur trioxide 117
Sulphuretted hydrogen 112
Sulphuric acid 113
Sulphuric anhydride 117
Sulphuric ether 176
Sulphurous acid 115
Sulphurous anhydride 114
Superphosphate 147
Symbols 76
Symbols, choice of 80
Symbols, table of 263
Symbols of commoner elements 76
Synthesis 25
Systems of crystals 110

Tallow 177
Tank waste 197
Tar 165, 178
Tartaric acid 178
Tea 184
Tellurium 122
Temperature, standard (normal) 45
Temperature of ignition 32, 170
Tempering of steel 224
Temporary hardness 213
Tension of aqueous vapor 48
Tetrabasic acids 122
Tetrad 95
Tetragonal system 110
Thein 184
Theophrastus 233
Theory 49
Theory, atomic 68, 70
Theory, molecular 41, 49
Theory of electrolytic dissociation 166
Thermite 238
Thiosulphuric acid 122
Thoria 213
Thorium 213
Tiles 239
Tin 239
Tin foil 240
Tin plate 240
Tincture 174
Tincture of iodine 99
Titanium 243
Tobacco 184
Transition temperature 111

PAGE
Transmutation 16, 232, 245
Triad 95
Tribasic acids 122
Triclinic system 111
Tungsten 248
Type-metal 118, 241

Universal solvent 16, 62
Upward displacement 132
Urea 161

Valence 94
Valentine, Basil 118
Value of study 13
Van Helmont 155
Vaseline 164
Verdigris 231
Vichy water 155
Vinegar 177
Vis vitalis 161
Vitriol, blue 232
Vitriol, green 225
Vitriol, oil of 118
Volumes of gases 44

Washing soda 198
Water 55
Water, distilled 64
Water, hard 212
Water, potable 63
Water of crystallisation 58
Water-gas 158, 165
Water-glass 199
Waters, natural 62
Weights, atomic 74
Weights, atomic, determination of 73
Weights, atomic of commoner elements 76
Weights, atomic, table of 263
Weights, molecular 51
Weights, molecular, determination of 51
Weldon's process 89
Welsbach, Auer von 243
Whey 180
Whiskey 175
White arsenic 142
White lead 242
Wines 175
Wintergreen, oil of 177

PAGE

Wöhler 161, 237
Wood, distillation of 172
Wood alcohol 172
Wood ashes 200, 201
Wood-pulp 180
Wood spirit 172
Wood's fusible metal 119
Wrought iron 222

Xenon 131

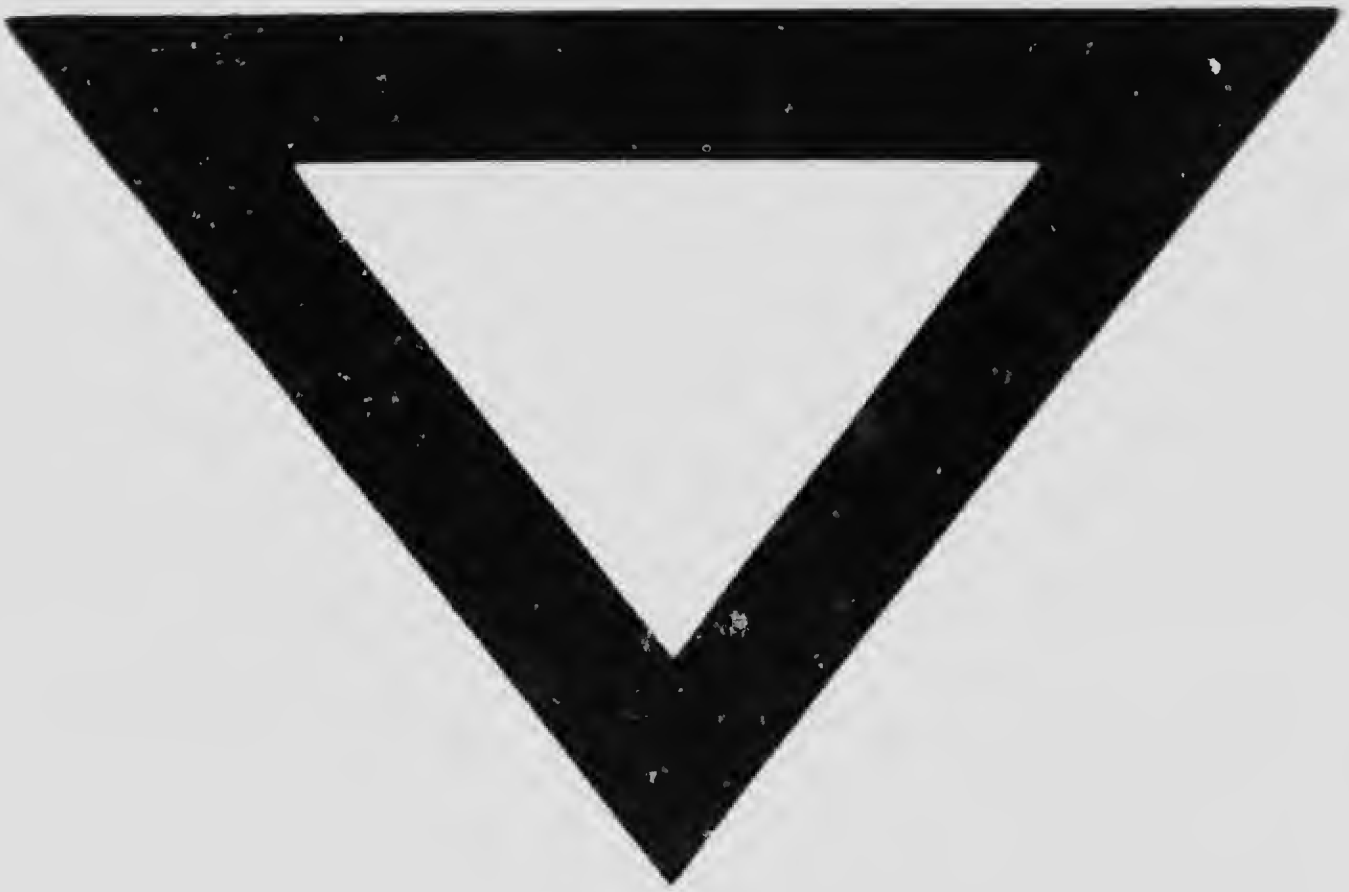
PAGE

Yeast 173
Yellow phosphorus 143

Zinc 236
Zinc blende 236
Zinc carbonate 236
Zinc hydroxide 237
Zinc oxide 237
Zinc sulphide 236
Zinc white 237
Zirconium 243

TABLE OF THE ELEMENTS

With Symbols and Atomic Weights

Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.9	Neon	Ne	20.2
Arsenic	As	74.9	Nickel	Ni	58.7
Barium	Ba	137.4	Niton	Nt	222.4
Bismuth	Bi	208	Nitrogen	N	14
Boron	B	11	Osmium	Os	190.9
Bromine	Br	79.9	Oxygen	O	16
Cadmium	Cd	112.4	Palladium	Pd	106.7
Cæsium	Cs	132.8	Phosphorus	P	31
Calcium	Ca	40	Platinum	Pt	195.2
Carbon	C	12	Potassium	K	39.1
Cerium	Ce	140.3	Praseodymium	Pr	140.6
Chlorine	Cl	35.5	Radium	Ra	226.4
Chromium	Cr	52	Rhodium	Rh	102.9
Cobalt	Co	59	Rubidium	Rb	85.5
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.6	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152	Silicon	Si	28.3
Fluorine	F	19	Silver	Ag	107.9
Gadolinium	Gd	157.3	Sodium	Na	23
Gallium	Ga	70	Strontium	Sr	87.6
Germanium	Ge	72.5	Sulphur	S	32
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4	Terbium	Tb	159.2
Hydrogen	H	1.008	Thallium	Tl	204
Indium	In	114.8	Thorium	Th	232.4
Iodine	I	126.9	Thulium	Tm	168.5
Iridium	Ir	193.1	Tin	Sn	119
Iron	Fe	55.8	Titanium	Ti	48.1
Krypton	Kr	82.9	Tungsten	W	184
Lanthanum	La	139	Uranium	U	238.5
Lead	Pb	207.1	Vanadium	V	51
Lithium	Li	6.9	Xenon	Xe	130.2
Lutecium	Lu	174	Ytterbium	Yb	172
Magnesium	Mg	24.3	Yttrium	Yt	89
Manganese	Mn	54.9	Zinc	Zn	65.4
Mercury	Hg	200.6	Zirconium	Zr	90.6