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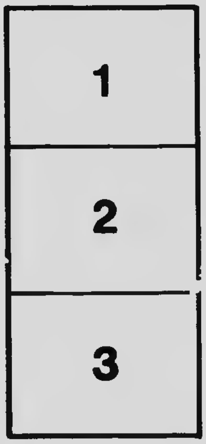
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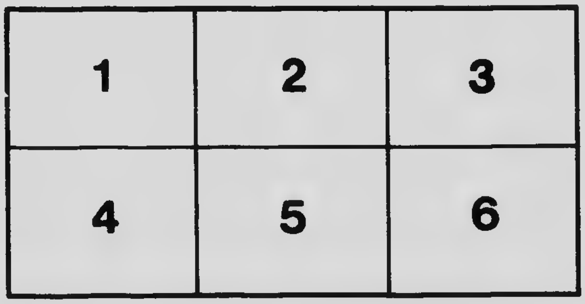
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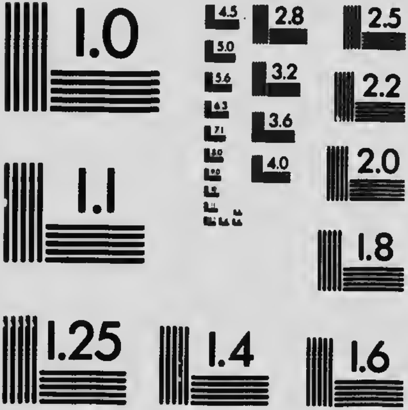

CHEMISTRY

HENRY CAVENDISH (1731-1810)

English chemist and physicist. Although one of the wealthiest men in England, he devoted himself to scientific pursuits and excluded every other interest. His extreme shyness and sensitiveness kept him from mingling with his fellows, even with men of science. "He probably uttered fewer words in his life than any other man who ever lived to four-score years." His experimental work was marked by extreme accuracy, skill, and perseverance. His most notable experiments were with gases, especially hydrogen, the discovery of which led to a new field of ever-growing interest, namely, experiments with balloons and aerial navigation. He was the first to demonstrate that water could be formed from the union of oxygen and hydrogen.

THE ONTARIO HIGH SCHOOL CHEMISTRY

BY

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PREFACE

There are certain essential features that every elementary text-book in Chemistry should exhibit.

(1) The chief function of science, as a part of school education, is not to impart information, but to offer a training in the scientific method by which the mind works up the concrete facts of nature into generalizations. Hence a text-book should show how investigations are conducted; and, for this purpose, the method by which the process of combustion and the composition of air and of water were discovered are presented with some detail.

(2) An elementary text-book should also state some of the generalizations or laws of chemistry, as it is a knowledge of these that indicates clearly that chemistry is a science. Moreover, it is essential, in order that these laws should be properly understood, that a knowledge of important substances, their methods of preparation, and their properties should be stated, as it is only by means of such knowledge that the generalizations can be approached.

(3) Side by side with the advance in the knowledge of the facts of chemistry has moved the development of chemical theories, and no adequate knowledge of the methods of chemistry could be presented without a statement of those theories that have had, and still possess, such potent influence on the advancement of the science.

(4) Chemical facts play so important a part in the industries and in the simple phenomena of daily life that it is necessary to show at every stage the application of

the chemical laws to the explanation of these facts. The Great War has shown so forcibly the predominant importance of the technical applications of chemistry that this phase of the subject is bound hereafter to be more strongly emphasized in elementary text-books.

(5) There is another phase of the subject which this volume has endeavoured to emphasize more than is usual in elementary text-books. While the facts of science are impersonal and are capable of being understood and appreciated by every normal mind, there is nevertheless a human side to science that the elementary text-book should not ignore. As facts of chemistry are glibly stated, it should never be forgotten that behind every fact is the long, tedious research by which that fact was discovered. The process of combustion, for example, which seems so simple to us, required 150 years of investigation by the keenest minds of Europe before it was finally elucidated by Lavoisier. A chemical fact assumes a new importance to the young pupil when he realizes that a great mind was willing to spend a lifetime in discovering it. Accordingly, pupils should be led to feel that the laboratories, as well as the battle-fields, have produced their heroes. In order to develop this human side of science many references have been made to the work of great investigators; and such classical experiments as those of Lavoisier on combustion and of Dumas and of Morley on the composition of water have been described, and illustrated with drawings of their original apparatus. In addition, portraits of eight of the most eminent chemists will be found in the book, together with brief biographical notes. It is hoped that the knowledge of the patient, unselfish labours of these men may develop in the pupils a desire to contribute something toward the advancement of science.

Many of the illustrations have been drawn for this book by the senior author. The original drawings of some of the early classical experiments have been reproduced, in order that the nature of the apparatus used in different stages of the development of chemistry should be known. The remaining illustrations are taken from such well-known texts as Roscoe's *Treatise on Chemistry*, Kahlenberg's *Outlines of Chemistry*, and Gregory and Simmon's *Lessons in Science.*

The authors are deeply indebted to a number of friends who have contributed in various ways to the volume. Very special thanks are due to Frank B. Kenrick, Ph.D., Associate Professor of Chemistry in the University of Toronto, who has gone very carefully through the text, giving invaluable assistance.

The authors will be pleased to receive any criticisms or suggestions by which the book in a future edition may be made more useful.

Toronto,
April 15th., 1917.

CONTENTS

CHEMISTRY

CHAPTER I

BURNING OF SUBSTANCES IN AIR

"The principle (substance) which unites with metals during calcination, which increases their weight, which brings them into the state of calces, is nothing else than the purest and most salubrious portion of the air; so that, if the air that has been entangled in combustion with a metal again becomes free, it comes forth in a very respirable condition, and more fitted than atmospheric air for maintaining the inflammation and the combustion of bodies."

—*Antoine Laurent Lavoisier, 1775*

1. Early study of combustion.—Among the various changes that take place in substances, some have attracted the attention of close observers from very early times. Plants appear to absorb earthy materials from the soil and to convert them into the substance of their tissues; animals eat the vegetable tissues and convert them into flesh and bone; both plants and animals die, and the materials of their bodies decay and apparently pass away into almost nothing. When coal, alcohol, and sulphur are burned, the first leaves only a very small amount of material behind as ash, while the latter two entirely disappear; metals placed in an open vessel and heated strongly lose all their lustre, and are converted into substances markedly different in appearance and properties from the original metals. While some attempt was made to investigate the changes in plants and animals, the processes of burning and heating metals claimed the chief attention of investigators during the early history of chemical research, and it may be said that for 150 years, from the middle of the seventeenth to the end of the eighteenth century, the study of combustion held the field as a subject of research.

Accordingly the heating of substances or *calcining*, as it was called by the early chemists, which formed the chief topic of study during the infancy of chemistry, will naturally form a fit beginning for the study of chemistry in school.

2. Burning of substances in air.—The changes produced by burning are certainly striking enough to attract the attention and provoke the wonder of the student. A piece of wood or coal is placed in the fire; gradually it becomes red-hot; flames of a brilliant red and orange colour appear, and smoke passes upward; the wood or coal diminishes in size, and finally nothing but a small part of the former amount of material is left, and that of a totally different character from the original wood or coal. In striking contrast with the wood and coal, this ash is gray and earthy, and crumbles to a powder when it is touched. No wonder such remarkable changes compelled the attention of the early chemists. Charcoal, also, when heated, glows and burns with scarcely a sign of a flame. Liquids like kerosene, turpentine, and alcohol burn with a flame, but, unlike wood and coal, leave no trace of ash behind. The gradual accumulation on the lamp chimney indicates, however, that other substances are formed when kerosene burns. Again, everybody has seen either natural or artificial gas of some kind burned, in a stove or for lighting purposes. In some of these cases of burning there is good evidence that other substances besides the ash or residue are formed. When coal and wood are consumed in a stove, the smoke rises from the chimney, soot collects within the stove pipes, and, in the case of coal, a poisonous gas sometimes escapes. When charcoal burns, there is no soot and little remaining ash, but the fact that, if it burns in a closed room, the atmosphere will soon poison a person present, is a certain indication that one or more poisonous gases have been produced by the combustion. The foregoing, and many other similar experiments, have led chemists to the general conclusion that when substances burn they disappear, producing other substances, which are left behind or pass off into the air as gas or smoke. In many cases also, as in the case of all the foregoing substances, the burning is accompanied by heat and light, and frequently by flame.

3. Calcination of the metals.—But many other substances, when heated strongly, act somewhat differently. If a piece of iron whose surface has been cleaned is placed in a flame, it becomes warm, then red-hot, but does not appear to burn like the substances already described. But after it has been removed from the flame and has become cool, the appearance of the metal will be entirely changed. The bright, metallic surface is now of a dark and dull colour, and if it is scraped with a knife, comes off in scales, quite brittle and totally unlike iron. In other words the surface is no longer iron, but a new substance; and if this outer covering is scraped off, it will be evident that only the surface has been changed, and that the interior is still iron. Moreover, if this newly exposed surface is placed in the flame, it also becomes coated with the same scaly substance. If this is again scraped off, and the heating repeated, gradually more and more of the iron is changed into the new substance, and it is quite possible by repeating the process to convert finally the whole of the hard, metallic iron into a pile of a dull, black, brittle substar Again, if instead of placing the iron in a flame, it placed in a crucible, the same changes take place. Copp lead, tin, and zinc, act in a similar manner when heat copper becomes a dull, black mass; lead turns to a yello crystalline solid; tin and zinc produce a white, loose ma magnesium and phosphorus, when heated in a crucib are converted into white substances, but during t process they glow brilliantly, producing much heat ar giving off dense, white fumes. The conversion the other metals into new substances is also accor panied by heat, but as only a small film on tl surface is changed, the amount of heat produced is no great enough to warm them to a temperature suffic ently high to make them glow. If the piece of iron converted into a very fine powder, this process increase its surface many times. Now, if this powder is place in a crucible, the surface of each grain is converted int another substance, and enough heat is produced to mak the whole mass glow with a dazzling light. By th application of great heat, zinc, lead, and tin may also b made to burn with a brilliant light.

4. Air and combustion.—But there was one factor to which the old chemists did not give due consideration in the study of the process of burning. They generally forgot that all these substances that were being heated and changed were in contact with the air. The pupil must not make the same mistake in his experiments and ignore the presence of the air, around everything with which he works. Indeed, the air being invisible and so universally present, is likely to be forgotten, and, as a result, phenomena in which it plays a part may not be properly understood. The most casual observation suggests that the air may play a part in the burning and calcination. In order that fuel may burn properly, a good draught of air must pass over the burning body; if this draught is checked, the coal or wood burns less vigorously, and if it is cut off entirely, the fire goes out. If magnesium is heated in a covered crucible, whenever the lid is raised and fresh air replaces the gas within, the metal flashes up brightly, as if it were burning with renewed vigour. Glowing coals, if covered with ashes so that there is little access of fresh air, burn very slowly or even become extinguished before they have been completely turned to ash. All these facts compel the conclusion that air does play a part in the process of burning. It will, therefore, be necessary to examine this process more carefully.

5. Increase of weight during combustion.—Consider again the case of the substances heated in the crucible. One of three things may have happened: (1) They may have been decomposed by the heat, part of the substance passing off and the residue remaining; (2) they may have united with something to form a new substance; or (3) the metal may have changed into the new substance without uniting with anything on the one hand or giving off any product on the other. It is quite possible to find out which of these three things has happened, for if the first process has taken place, then the weight of the residue will be less than that of the substance heated; if the second, its weight will be greater; and if the third, it will not have changed in weight at all. All that one needs to do is to weigh the crucible and its contents, both before and after heating it. In an experiment tried with copper filings, the weight of the crucible and filings before heating was 27.522 grams, and after heating 27.693 grams, indicating an increase in weight of .171 grams. Iron, lead, and tin also increase in weight. Phosphorus and magnesium also increase, if care is taken that none of the substance formed escapes. When a candle burns, there seems to be no residue left, but if all the substances formed are collected, it is found again that the products of combustion are heavier than the candle itself; the products are gases, and special arrangements are necessary to collect them. In the same way, wood, kerosene, and, in fact, all substances can be proved to increase in weight when they burn. This increase in weight the early investigators of combustion either did not observe, or they treated it as of no importance; for they made little use of the balance and did not put much stress on the weight of bodies. The neglect to consider the importance of the balance prevented for many years the solving of the problem of combustion, and it was not until Lavoisier began measuring the quantities of substances in reactions, that the problem was fully solved in a manner to be described.

If a metal in a crucible, when heated, increases in weight, the increase must have been produced by the absorption of some substance from the air or from the flame, on the part of either the crucible or the metal. It can easily be shown by heating the crucible alone that it is the metal and not the crucible that has increased in weight. Since the crucible remains unchanged, it is hardly possible that the gases of the flame passed through the crucible to unite with the metal within. So we are driven to the conclusion that when substances burn or are heated in the air, they unite with at least a part of it. That, however, these substances, when heated without air contact, remain unchanged, is easily demonstrated by placing the combustible substance in a crucible, covering it with sand or bone-ash, and heating it. When the sand is removed, the substance is seen to be almost unchanged, any slight superficial discolouring being due to the small quantity of air that occupied the spaces among the particles of sand. Moreover, there is no change in the weight of the substance.

6. Heated substances absorb from the air.—Do those substances that react with the air in burning, unite with the whole of the air or with only a part of it? In order to answer this question, it will be necessary to heat the substances in a confined quantity of air, and to measure what part of the air has disappeared.

The substance can best be placed in a gas bottle, which is tightly corked, and then heated. Iron, copper, or magnesium would not be very suitable, as the heat necessary to convert them rapidly into a new substance is likely to break or melt the bottle, but phosphorus kindles at a low temperature, and if the bottle is heated uniformly, there is only slight danger of breaking it. A piece of phosphorus as large as a pea is placed on asbestos in the bottle, which is then tightly corked and heated gently on all sides until the phosphorus begins to ignite. The bottle becomes filled with dense white fumes, and soon the flame goes out, leaving some brown deposit behind. The bottle is allowed to cool, and the mouth is thrust under water. The cork is now withdrawn, and the water rushes in until it fills about one fifth of the bottle. The bottle is then taken out of the water, a burning splint is quickly inserted into it, and, at once, the flame is extinguished. If, however, the splint is inserted into a bottle filled with ordinary air, it continues to burn for a short time.

This experiment indicates that the air remaining in the flask is not ordinary air, but that the part which supports the combustion of the splint has largely disappeared. It might be considered possible that this change in the property of the air is due to the fact that phosphorus, in burning, produces a gas that mixes with the air, and thus affects its properties. But the most careful study of the burning of phosphorus in air has led to the conclusion that no such gas is produced, the white cloud being the only product of combustion. As this cloud is composed of small, solid particles, these soon settle down on the sides of the vessel and leave the air above quite clear. If the brown substance left in the flask after the phosphorus became extinguished is taken out and heated, it soon ignites and continues to burn, indicating that it is phosphorus that was left unburned in the air. The explanation of this phenomenon is that the phosphorus went out, not because it was all consumed, but because the part of the air with which it unites had become largely exhausted. This experiment and many others of a similar nature have led to the conclusion that air is made up chiefly of two components, one of which unites with substances when they burn, and the other of which will not support combustion. The foregoing experiment also indicates that the noncombustible component of air occupies about four fifths of its volume.

7. Decomposition of calcined mercury.—If this interpretation of the phenomenon of burning is correct, the black products from heating iron and copper, and the white products from heating zinc, magnesium, and phosphorus contain two constituents, namely, the original substance and a component of the air. It should be possible to separate each product again into its constituents, and it would be of great interest to obtain this active component of the air free from the other inactive part. Fortunately the product left after calcining mercury lends itself readily to this treatment. Mercury or quicksilver had a great fascination for the early chemists, as, indeed, it has for the modern school-boy. Its great weight and buoyant power, and its beautiful silver lustre are striking and interesting, and many experiments may be performed with it. It was early

JOSEPH PRIESTLEY (1733-1804)

English theologian and chemist. The early part of his life was devoted to theological studies and controversy, and it was not until he was nearly forty that he began his experiments in chemistry. He developed great ingenuity in devising apparatus, but lacked skill in manipulation. He also lacked power to analyse his experiments thoroughly and push them to their logical conclusion. Hence he is credited with the discovery of no great chemical laws. His high rank as a chemist rests on the important gases he prepared and collected. These included oxygen, hydrogen, chlorine, ammonia, and sulphur dioxide. He also discovered the interdependence that exists between animal and plant respiration. In 1794 he removed to the United States, where he died.

learned that, when heated in the air, it gradually turned into a red powder. This red powder was called *mercurius calcinatus*, or calcined mercury. When raised to a still higher temperature it decomposes, mercury is condensed on the sides of the containing vessel, and a gas escapes from the tube. The decomposition of this red powder was first carried out by Joseph Priestley, one of the ablest chemists of the eighteenth century.

Priestley filled a small flask with mercury (Fig. 1) and inverted it in a vessel of mercury; then he put the red powder under the mouth of the flask, whereupon the powder rose through the heavy mercury to the top. Then, in his own words, "having procured a lens (L) of twelve inches diameter, and twenty inches focal distance, on the first of August, 1774, I endeavoured to extract air from mercurius calcinatus (calcined mercury); and I presently found that, by means of this lens, air (gas) was expelled from it very readily."

The lens was used to focus the sun's rays, which gave the great heat necessary to decompose the substance.

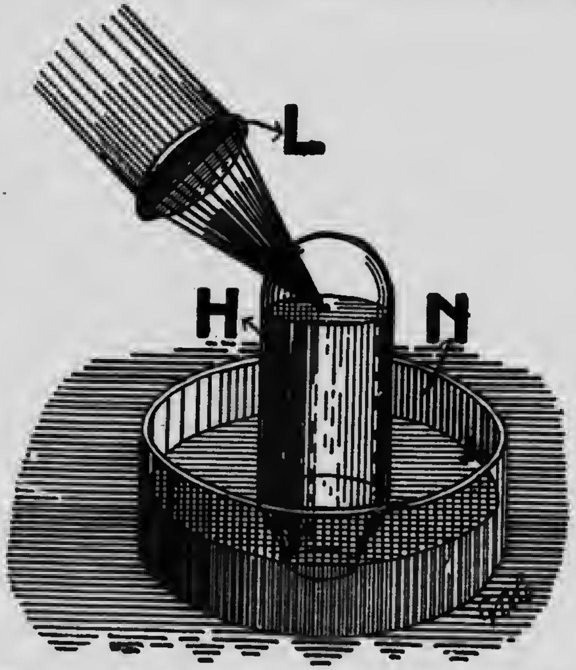

Fig. 1.—Priestley's Apparatus for Preparing Oxygen from Mercuric Oxide

H. Flask of mercury with mercury oxide floating on top.
L. Large burning glass or lens.
N. Pneumatic trough.

The gas which was produced, and which was recognized as a component of the air, was found to have remarkable properties, and was called by him "dephlogisticated air." Later, it was named *oxygen*, the inactive component of the air being named *nitrogen*.

8. Lavoisier's great experiment on combustion.—The complete explanation of combustion was finally given by the founder of modern chemistry, Antoine Lavoisier, a brilliant French investigator, who perished in 1794 by the guillotine at the hand of the Revolutionists. His experiment, which finally settled the matter, was probably the most notable in the history of chemistry. Figure 2 is a drawing of the original apparatus.

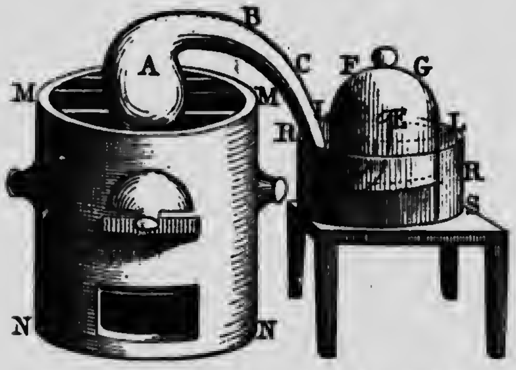

Fig. 2.—Lavoisier's Original Apparatus for Finding the Composition of Air

A. Glass retort containing mercury.
F.G. A bell-jar containing air. It stands in a jar, R, containing mercury. M. Charcoal furnace.

Priestley had told him of his success in breaking up calcined mercury into mercury and dephlogisticated air. As will be seen from the illustration, Lavoisier took a retort and bent up the neck, so that it reached into a glass bell-jar placed with its mouth immersed in mercury. The air in the bell-jar and in the retort were in communication. He put mercury into the retort and placed a charcoal fire beneath it. Nothing happened the first day; during the second, little red particles were seen swimming over the surface, and these increased until the fifth day, but not after. During the same period the mercury rose in the bell-jar and ceased rising at the same time as the red particles ceased increasing. He found the decrease in the volume of air in the bell-jar to be 7½ cubic inches. He gathered the red powder off the surface of the mercury and weighed the quantity of mercury remaining. He now heated the red powder, collecting the gas that came off, and found that its volume was

ANTOINE LAURENT LAVOISIER (1743-1794)

French chemist. After leaving the College Mazarin, where he had a brilliant career
as a student, he devoted himself to the study of chemistry and mathematics. In
1766 he gained the prize offered by the French Academy of Science for an improved
method of lighting the streets of Paris. He systematized chemical research and laid
the foundations of modern chemistry. He was one of the first to prepare oxygen;
he uprooted the phlogistic theory and declared combustion to be the union of the
combustible substance with oxygen. He discovered the constituents of various acid
and metallic oxides and of numerous animal and vegetable substances. A man of
wealth and high official position under Louis XVI., he brought about many reforms
in the financial policy of the Monarch and in the levying of taxes. He introduced
the potato and the sugar beet into France and improved the methods of agriculture.
As director of the government powder-mills he improved the mode of manufactur-
ing gunpowder. Despite his many services to the state, he became disliked during
the French Revolution, was imprisoned, and sentenced to death. The guillotine put an
end to the life of one of the greatest men of science the world has produced.

the same as the decrease of air in the bell-jar, namely, 7½ cubic inches, thus proving conclusively that the mercury had absorbed a component of the air and that heating the red powder gave back that component in equal quantity. Moreover, he found that the loss in weight of the mercury in the retort after heating, namely, 41½ grains, was just equal to the weight of the mercury recovered by heating the red powder. This explanation of combustion started modern chemistry on the road of progress along scientific lines.

Our final conclusion is that many substances, when heated in air, unite with one of its components, oxygen, to form new substances. Names are given to many of these new substances which indicate their composition. The white ash obtained from magnesium is magnesium oxide, the red ash from mercury is mercuric oxide. Zinc oxide, tin oxide, and iron oxide are the names of the products obtained by heating the respective metals.

When the two main components of air were discovered, and the important role played by one of them, oxygen, in many of the best known processes about us was made clear, the investigation of the properties of the gases, oxygen and nitrogen, was undertaken with renewed zeal. This study of the air and its components will be undertaken in the next chapter.

QUESTIONS

1. Would you classify smoke as a solid, a liquid, a gas, or some combination of these? Give reasons.

2. State why we consider magnesium ash to contain something derived from the air.

3. You wish to find, by removing the oxygen, the proportion of nitrogen in a corked bottle full of air. Which would be more suitable for this experiment, phosphorus or magnesium? Give reasons.

4. Suggest a reason why magnesium and phosphorus are converted completely into their oxides when heated, while copper and iron are converted on the surface only.

5. Why does iron burn in oxygen, but not in air?

6. Bricks are made by shaping clay and then "burning" it. State, with reasons, if this is a proper use of the word "burning".

7. Why is yellow phosphorus kept under water?

8. How would you show that air is made of more than one substance?

9. The substances left by heating solids in air are sometimes heavier and sometimes lighter than the substances heated. Name two substances of each kind, and explain the difference in weight for each substance named.

10. The old chemists believed that when a metal was calcined it gave off a substance called phlogiston. How can it be proved that they were wrong?

11. Would iron rust more rapidly if it were freely exposed to the air, or if it were placed at the bottom of a vessel filled with fine sand? Give reasons for your answer.

12. When tin is heated in a corked glass vessel the metal becomes coated with a new substance. When the vessel is cooled and its mouth placed under water and the cork withdrawn, some water enters the vessel. Explain the phenomenon, and state what would happen to a burning splint which was lowered into the gas remaining in the jar.

CHAPTER II

AIR AND ITS COMPONENTS

OXYGEN

> "My reader will not wonder, that, having ascertained the superior goodness of dephlogisticated air (oxygen) by mice living in it, I should have the curiosity to taste it myself. I have gratified that curiosity by breathing it. . . . Who can tell but that, in time, this pure air may become a fashionable article of luxury. Hitherto only two mice and myself have had the privilege of breathing it."
>
> —*John Priestley, 1775*

9. History.—It has been already stated that John Priestley in 1774 produced oxygen by decomposing mercuric oxide, using as a source of heat the rays of the sun concentrated on the powder by means of a powerful lens (Fig. 1). It had undoubtedly been produced and recognized before that time, but had not been collected free from other gases, as the simple method of collecting gases over water or mercury had not long been discovered. K. W. Scheele, the brilliant Swedish chemist, had produced oxygen from saltpetre several years before Priestley used his magnifying-glass. Scheele collected it in bladders and called it "fire-air"; Priestley called it "dephlogisticated air"; and finally Lavoisier gave it its present name, oxygen, which means "acid producer".

10. Sources.—Oxygen is the most important of all gases. When it is considered that eight ninths of all the water, one half of all the rocks, and one fifth of the atmosphere, are composed of oxygen, its predominant importance is established. As all plants and animals are largely composed of water, they contain large quantities of oxygen; and even if they were heated in an oven until all the water was driven off, the dry part remaining would still contain a large proportion of oxygen.

11. Preparation.—One of the simplest methods of obtaining this gas is by heating mercuric oxide, as has been learned in Chapter I.

A small quantity of mercuric oxide is placed in the bottom of a long, narrow, hard-glass test-tube and heated strongly. The red oxide first becomes black, and then, as the heat is increased, a mirror forms on the cooler parts of the test-tube. If a glowing splint is inserted into the tube, the brilliant glow indicates that oxygen is coming off. Finally, if the mercuric oxide is pure, no residue is left, and the mirror breaks up into metallic globules of mercury, which run down to the bottom of the test-tube. Hence we see that mercuric oxide, when heated, is converted into mercury and oxygen.

In the foregoing paragraph it is stated that the mercuric oxide should be heated in a hard-glass test-tube. As so many chemical operations are performed in glass vessels, the pupil should know something regarding the qualities of glass.

One reason why glass is so largely used in chemical experiments is that nearly all the substances used in the laboratory have no action on it. It may, therefore, be considered as remaining passive in all experiments. In making laboratory glass-ware, two kinds of glass are used, hard glass and soft glass. The latter is more easily worked, and vessels made from it are cheaper. It is called soft glass because it melts at a comparatively low temperature, while hard glass will melt only at a very high one. On account of the cheapness of soft glass, beakers, flasks, and ordinary test-tubes are made of it, and, accordingly, they should never be heated strongly. Where intense heating is necessary, test-tubes or other vessels of hard glass are used.

Many other substances containing oxygen give off the gas when they are heated strongly, and usually leave a residue in the test-tube. Saltpetre, manganese dioxide, red lead, and potassium chlorate are examples of such substances. Yet it would be quite wrong to infer that all substances containing oxygen liberate this gas when they are strongly heated, for many do not. Magnesium oxide and phosphorus oxide, no matter how strongly they are heated, give off none of this gas.

In selecting a suitable laboratory method for the preparation of this gas, several things should be considered. A substance should be selected that gives off a large quantity of oxygen for every gram of the substance used; it should give off the gas freely at a low temperature, and the substance itself should be cheap. Mercuric oxide is too expensive. While manganese dioxide is cheap, it has to be heated very intensely, and it generates only a small quantity of oxygen per gram. Potassium chlorate is cheap, produces a large quantity of oxygen per gram when heated, and generates the gas at a medium temperature. If manganese dioxide is added to it, the gas comes off abundantly at a still lower temperature, and so a mixture of these two substances is always used as the source of oxygen for laboratory experiments.

12. Collection of gases.—When the mercuric oxide is heated, the oxygen is driven off and mixes with the air. In order that its properties may be accurately studied, the oxygen must be collected separate from other gases.

Chemists only gradually learned how to collect gases in a pure state. At first the substance to be heated was placed in a glass vessel, and the gases generated were examined in the generator itself. But all the gases produced were mixed up together with the air in the vessel, and it was very difficult to tell what properties were due to each gas. Stephen Hales, a noted English physiologist of the seventeenth century, was the first to separate the generator in which the gas was produced from the collector into which the gas was passed. He filled the collector with water, and inverted it in a vessel of water called a pneumatic trough, and then passed the gas up into the collector, where it replaced the water. Thus the gas could be obtained in a fairly pure state. Gases soluble in water could not be collected in this way, and Scheele used bladders for collecting such gases, but Priestley collected them over mercury instead of over water.

13. Preparation from potassium chlorate.—Figure 3 shows the arrangement of the apparatus for preparing and collecting the oxygen. The potassium chlorate and the manganese dioxide are placed in the tube and heated. The oxygen passes through the delivery tube and collects in the bottles by displacing the water.

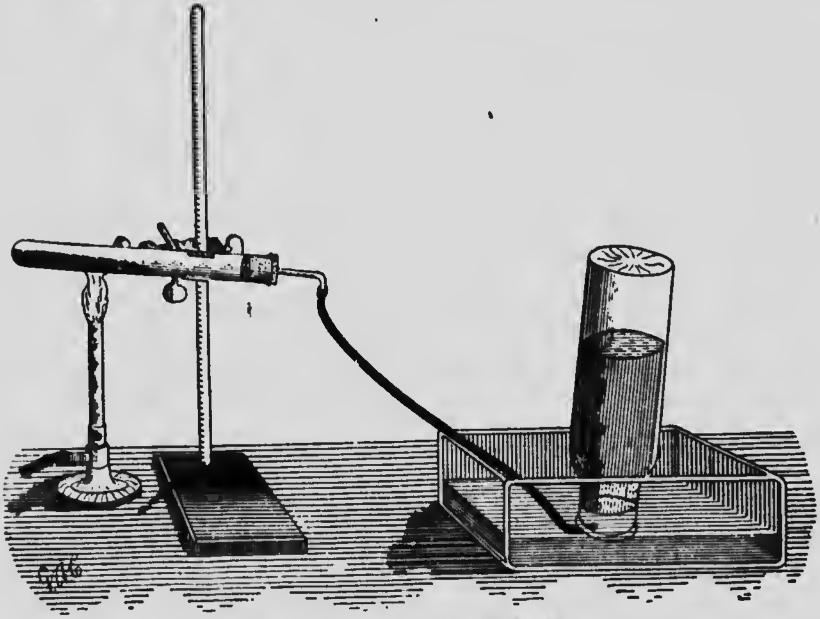

FIG. 3.—PREPARATION OF OXYGEN

14. Examination of the residue.—It has been found already that both potassium chlorate and manganese dioxide, when heated, produce oxygen, and in the foregoing experiment the two were heated together. We have to decide whether the oxygen came from one of the substances or from both. If each is weighed separately before the reaction, and its properties studied, and if the residue left after the oxygen has passed off is examined, it is found that the manganese dioxide is left unchanged. It can be separated from the other part of the residue by adding water to the test-tube and heating, as the manganese dioxide is left undissolved, while the other part of the residue dissolves quite readily. There is now in the test-tube a solution of one part of the residue and a black insoluble substance intermingled with the liquid. This insoluble substance is said to be ***suspended*** in the liquid. Such a substance is now separated from the liquid by a process called *filtration.* A porous paper is used for this purpose, and is usually placed in a funnel. The pores in the paper allow the liquid to pass through readily, but are too small to admit any of the suspended particles. The liquid that passes through it is called the *filtrate.* The residue left on the filter paper in this case has exactly the same properties as the original manganese dioxide, and if it is all collected and weighed, it will be found that there has been no decrease in weight. So we are justified in concluding that the manganese dioxide has remained unchanged throughout the experiment, and that none of the oxygen has come from it. If now the filtrate is evaporated, a white solid is left behind, which is quite unlike the potassium chlorate in taste, crystalline form, and in most other respects; moreover, its total weight is much less than that of the potassium chlorate originally used. This new substance is called ***potassium chloride.*** The conclusion reached is that all of the oxygen comes from the potassium chlorate, and that potassium chloride is left. This reaction may be expressed briefly in this manner:

Potassium chlorate⟶potassium chloride+oxygen.

The part played by the manganese dioxide in the foregoing experiment is peculiar. As we know already, the same reaction takes place when potassium chlorate is heated alone, but it must be raised well above its melting-point

(372°C.), before the oxygen begins to come off, while if manganese dioxide is added, oxygen is produced below 350° C. The effect of the manganese dioxide can be well demonstrated by heating some potassium chlorate in a test-tube until the salt is all melted and bubbles are rising through it, indicating that oxygen is being generated, but not rapidly. If a pinch of manganese dioxide is now dropped into the fluid mass, a violent ebullition at once takes place, indicating a much more rapid generation of oxygen. A substance acting as manganese dioxide does in this case, is called a *catalyst* or *catalyzer*, and the action is called *catalysis*. From these experiments we learn that a catalyst increases the rate of reaction, and is not itself changed during the reaction.

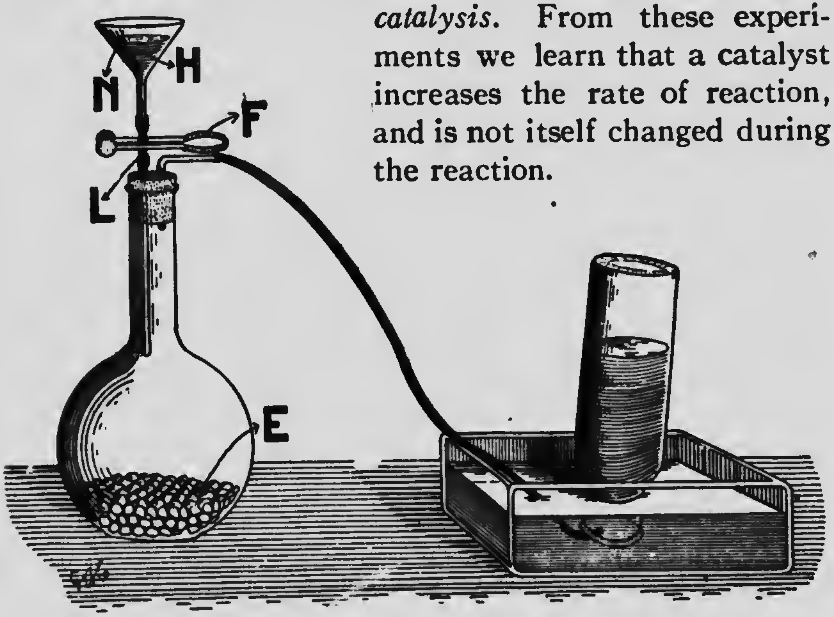

FIG. 4.—PREPARATION OF OXYGEN FROM SODIUM PEROXIDE AND WATER
E. Sodium peroxide. F. Pinch-cock. H. Water. L. Flexible rubber tubing. N. Funnel.

15. Preparation from sodium peroxide.—A third quite different method of preparing oxygen is by utilizing the action of water on a white solid called sodium peroxide. If apparatus is arranged as in the drawing (Fig. 4), the peroxide is put into the flask, and water is poured into the separating-funnel. The water is then allowed to pass down on the peroxide, one drop at a time, and the oxygen thus generated is collected by displacement of water. The water reacts on the sodium peroxide to produce oxygen and a white solid called sodium hydroxide or caustic soda. We can express the reaction thus:

Sodium peroxide+water→sodium hydroxide+oxygen.

16. Properties of oxygen.—This gas has neither colour, taste, nor odour, and like all other gases, it is perfectly transparent. It is only slightly soluble in water. If 1,000 c.c. of water at 0°C. had all the oxygen driven from it and collected, it would occupy 31 c.c. Though the quantity of oxygen dissolved in water seems small, it plays a very important part, as all fishes and other animals living in the water depend on it for purifying the blood. If water is boiled and thus freed from oxygen, a fish or other aquatic animal placed in it will rapidly drown. Oxygen is slightly heavier than air, for 1 litre of it at 0°C. and 760 mm. pressure, weighs 1.43 grams, while 1 litre of air under the same conditions weighs 1.29 grams. Oxygen, however, is absorbed very rapidly by a solution of pyrogallic acid and potassium hydroxide, so that, if the mouth of a vessel filled with oxygen is inserted into this solution, the latter rises rapidly to the top, and turns dark brown. This change of colour and absorption is a good test for oxygen.

All substances that burn in air burn more brilliantly in oxygen. If a splint of wood with a spark on the end is inserted into a bottle of oxygen, it will burst into a brilliant flame and continue to burn until the oxygen is all used. A gas is formed which dissolves in water. If the splint of wood is burned in a bottle of air the same gas is produced. Sulphur and phosphorus burn brilliantly in oxygen, the former producing an irritating gas, and the latter dense and white fumes, which soon settle on the bottom of the vessel. Both these products dissolve readily in water. Calcium, sodium, and magnesium burn brightly in oxygen, white solids being formed which also are soluble in water. No matter how intensely a piece of iron is heated in air, it does not ignite and burn; but, if you tip a piece of thin iron wire or watchspring with sulphur, ignite the latter, and insert the spring into a bottle of oxygen, the iron burns with sparkling brilliancy, producing globules of a black, brittle substance quite unlike iron. This substance is insoluble in water.

In every case the substances burned unite with the oxygen to form the product left in the bottle. The sulphur forms *sulphur oxide;* the phosphorus, *phosphorus oxide;* the magnesium, *magnesium oxide*; etc. When these substances burn in air, these same products are formed, but the burning is with much less vigour. The reason why substances burn with such increased intensity in pure oxygen is easily explained. As a substance burns in air or oxygen it produces heat. This heat is communicated to the unburnt part of the substance and to the gases close to where the burning is taking place. The hotter these are, the more intense will be the light and the more rapidly will the substance burn. When the substance burns in air, as only one fifth of this gas is oxygen, and as the heat produced by this quantity of oxygen uniting with the substance has to warm large quantities of the nitrogen of the air, the temperature never becomes high enough to make the burning rapid or the light intense.

The soluble oxides can be divided into two classes, those whose solutions are *acids* and those whose solutions are *bases*. Acids were given this name, because they all taste sour (*acer*, sharp). They may be detected by their taste, but chemists have devised safer and more accurate tests, one of which is the action of litmus. Litmus is a dye extracted from lichens in Holland. This dye is used as a solution in water, or porous paper is dipped into a solution of the dye and dried. Such a preparation is called litmus paper. Substances called acids turn blue litmus red: bases turn red litmus blue. Of the oxides already mentioned those formed by burning carbon, sulphur, and phosphorus, when dissolved in water, turn blue litmus red, and hence their solutions are acids. On the other hand, the oxides of calcium, magnesium, and sodium, when dissolved in water, turn red litmus blue, and hence their solutions are bases. The substances whose oxides produce the bases are all bright, have a metallic lustre, and have other properties in common. They are called *metals*. On the other hand, those whose oxides produce acids have not these properties and are called *non-metals*.

17. Commercial importance.—When Priestley discovered oxygen nearly one hundred and fifty years ago, he asked: "Who can tell but that in time this pure air may become a fashionable article of luxury?" He kept mice in this new gas, and because of their great activity, he believed oxygen to have an exhilarating effect on animal life, and looked forward to the time when the wealthy would use it for producing this effect upon themselves. But it is now known that if it were used for that purpose, breathing would cease altogether and oxygen poisoning would result However, Priestley's prophecy has been partially fulfilled, for oxygen is now used largely in hospitals in cases of pneumonia, asthma, and coal-gas poisoning, and for artificial respiration in cases of drowning, and of suffocation from smoke and other causes. In submarines and diving-bells it is also largely used, diluted with nitrogen. During the last few years two very considerable uses have been made of oxygen in the industrial world. The oxy-acetylene flame is by far the most effective heating agent for welding; many joints can be welded by this means that formerly had to be riveted. This flame is produced by burning a mixture of oxygen and acetylene at the end of a nozzle. The other use is for cutting iron. We have seen that hot iron burns in oxygen. If a gas flame plays on a piece of wood, it will in time burn a hole through it. If the flame is moved slowly across the wood, the latter will soon be cut in two. Similarly, if a thin jet of the oxy-acetylene flame plays against a piece of iron, the iron will burn like the wood, and a clean cut can be made through the hardest armour-plates, twenty-four inches thick, at the rate of one foot in five minutes or less. As iron plates can be cut along any line, whether curved or straight, one can easily see how extensive may be the application of oxygen in this direction. Probably 500,000,000 cubic feet of it are used industrially each year, and this use of oxygen is yet in its infancy.

The growth of the industrial use of oxygen is due to the fact that the price of manufacturing it has greatly decreased within recent years, until now it can be produced at about 1 cent. per cubic foot. The commercial method of production will be considered after the chemistry of nitrogen has been described.

NITROGEN

> "The gas, nitrogen, serves as a blanket to keep the world from burning up in the oxygen of the atmosphere. . . . The slightest fire could start a great and overwhelming conflagration. A single touch might commence the conflagration of the world."
>
> —*Hollis Godfrey*

18. History.—In 1772 Dr. Rutherford, a learned Scottish professor of botany, found that when mice were kept in a vessel of air until they died, and the gas they exhaled was absorbed by alkali, there remained a gas of a smaller volume than the original air. This residual gas he called "phlogisticated air." He also studied some of its properties. Lavoisier, who extracted the oxygen from the air by mercury, as we have seen, (Fig. 2), called the remaining component of the air "azote", meaning, "not having life", in reference to the fact that it does not support life. Later it was called nitrogen, because it was found to be a constituent of nitre, or saltpetre.

19. Sources.—The chief source of nitrogen is the atmosphere, which contains about 78 litres of nitrogen in every **100** litres of air. It is not an important component of the earth's crust, but it is found in Chili saltpetre, of which there are extensive beds in Northern Chili. It is an important constituent of the guano found on desert islands in the Southern Ocean. Besides, it forms an essential element of the living parts of all organisms, from the most lowly germs to the giant trees and to man himself. When plants and animals decay, nitrogen is always found in the products of their decomposition.

20. Preparation.—As air contains nitrogen in immense quantities, and as the other main component of air is oxygen, the method that naturally suggests itself for preparing nitrogen, is by separating the oxygen from the air, and in fact this is one of the best methods of obtaining nitrogen. Arrange the apparatus as in Figure 5. In the horizontal hard-glass tubing are placed either copper turnings or iron filings, and the tube is heated until the metal in it is red-hot. The air is forced through the apparatus by pouring water slowly down the funnel. During its passage over the red-hot metal, this metal combines with the oxygen of the air, and nitrogen is collected over water in a gas bottle.

Iron unites with the oxygen of the air, not only when it is hot, but even when it is cold, if the air is moist. The iron withdraws the oxygen, and turns into rust; hence it is only necessary to tie iron filings loosely in cheese-cloth, place them in a bottle of air with its mouth under water, and all the oxygen will be taken from the air. But the action will be much slower than if the iron were hot. Red-hot iron will take all the oxygen out of a quantity of air in a few minutes, while iron at the temperature of the room may take several days to extract the oxygen from the same quantity of air. Carbon or sulphur could not be used instead of iron or copper, for while they unite readily with the oxygen, they form gaseous substances, as we have already learned, and the nitrogen would be mixed with these gases. However, it would be quite possible to get rid of these impurities by adding substances that would absorb the former. In Rutherford's experiment, referred to in Section 18, the impurity mixed with the nitrogen was the gas exhaled by the mice. To this he added alkali which quickly absorbed it, and the nitrogen was left.

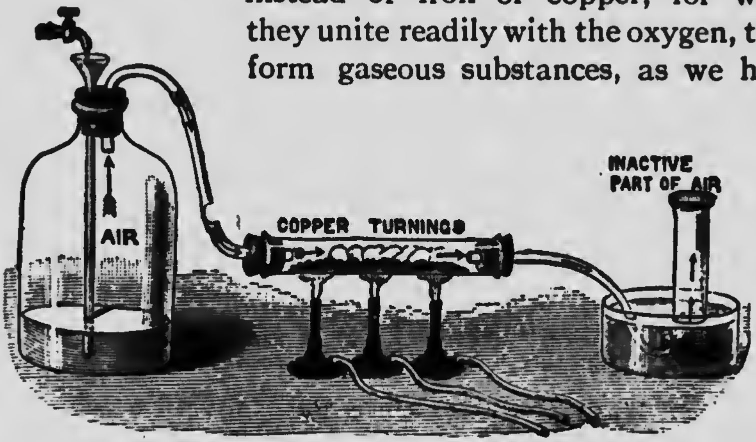

FIG. 5.—METHOD OF PREPARING NITROGEN FROM AIR

Nitrogen can be prepared from other substances besides air. If sodium nitrite and ammonium chloride, both of which contain nitrogen, are mixed and then dissolved in a little water in a flask, and heated gently, nitrogen bubbles off in a steady stream, and can be collected over water. This is the best laboratory method of preparing nitrogen, and produces a purer gas than the method of producing it from the air as already described.

21. Properties.—Nitrogen has no smell or taste. It is colourless and is only slightly soluble in water, as its method of collection shows, one litre of water at 0°C. dissolving 24 c.c. of nitrogen. It is not so heavy as oxygen, 1 litre of it at 0°C. and 760 mm. weighing 1.250 grams. It can be converted into a liquid as clear and colourless as pure water.

If a piece of burning phosphorus or a blazing splint is plunged into a jar of this gas, the flame is at once extinguished, and all action ceases. The same happens to burning sodium, calcium, and sulphur. It is quite different, therefore, from oxygen in this respect. Only with difficulty can it be made to unite with magnesium and calcium.

In the horizontal, hard-glass tube (Fig. 6) is placed some powdered magnesium in a porcelain boat. Pure nitrogen is passed through it from right to left until all the air is expelled from the apparatus. Then the tap is turned, and the hard-glass tube is heated strongly. At first nitrogen bubbles through the coloured water owing to the expansion of the gas by the heat, but this ceases when the magnesium reaches 900°C. and the coloured

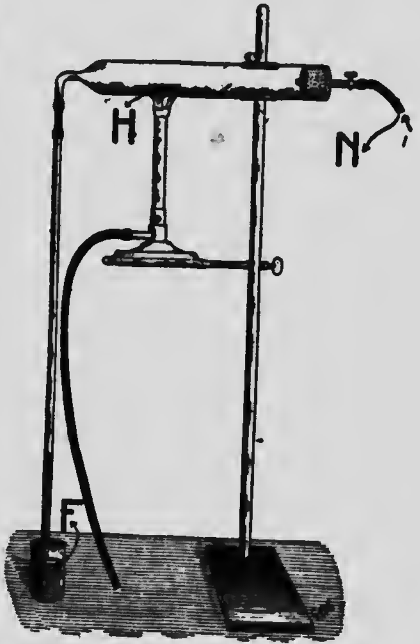

FIG. 6.—APPARATUS TO SHOW COMBINATION OF MAGNESIUM AND NITROGEN
F. Coloured water.
H. Magnesium powder.
N. Tube for entrance of nitrogen.

water begins to rise in the tube, indicating that some of the nitrogen is being absorbed. An examination of the magnesium will show that it has changed its appearance.

The substance formed when magnesium unites with nitrogen is called *magnesium nitride*, just as its compound with oxygen is called magnesium oxide. Calcium with nitrogen forms calcium nitride, and other *nitrides* can be formed in a similar manner.

We say that nitrogen is an inactive substance, meaning that it does not readily act on other substances. But recently it has been found that when an electrical discharge is passed through the pure gas, the latter becomes very active. Phosphorus then combines violently with it, iodine burns in it with a beautiful blue flame, and sulphur also burns in it with vigour.

22. Uses.—Up to quite recent times nitrogen has been used to a very small extent, and at the present time its chief commercial use is for filling the bulbs of electric lamps.

We have said already that every plant contains nitrogen, yet none of our green plants are able to utilize the nitrogen of the air. Though they have their roots, stems, and leaves in immediate contact with the billions of tons of nitrogen in the atmosphere, they would starve to death for want of nitrogenous food unless the soil

Fig. 7.—Root of a Leguminous Plant Showing Tubercles

contained other nitrogenous materials than air. Some few plants are able to feed directly on the nitrogen of the air, but they are of a very low type, being bacteria. Peas, beans, clovers, vetches, and a few other plants can thrive in a soil that contains no nitrogenous material except air. If these plants are carefully pulled up, numerous little swellings called nodules (Fig. 7) are found on their roots, and, when these nodules are examined under the microscope, they are found to be teeming with bacteria; these convert the nitrogen of the air into other substances, which the higher plants are able to use as food. As the stock of nitrogenous foods for plants is being used as manures much more rapidly than it is being manufactured in nature, many endeavours have been made to convert the atmospheric nitrogen into substances that can be used as manures. In recent years

FIG. 8.—BIRD'S-EYE VIEW OF THE CYANAMIDE FACTORY AT NIAGARA FALLS, ONTARIO
(This is the largest chemical industry in Canada)

success has been achieved, and now a manure called *calcium cyanamide* is formed by passing nitrogen over heated calcium carbide, and is being manufactured in large quantities in various countries. A very large factory for the manufacture of this fertilizer is situated at Niagara Falls, Ontario (Fig. 8), with numerous buildings covering forty-two acres, and employing almost 2,000 workmen. This is the largest chemical industry in Canada, the annual capacity of the factory being 64,000 tons of cyanamide.

AIR

23. Composition.—Air, as we have seen, is composed chiefly of the gases, oxygen and nitrogen. One hundred litres of air contain about 79 litres of nitrogen (including argon) and 21 litres of oxygen, while 100 grams of air contain about 77 grams of nitrogen and 23 grams of oxygen. We have learned already how Lavoisier found the approximate composition both by weight and by volume. The usual method of finding the percentage composition by volume is to measure a volume of air, then to extract the oxygen from it, and finally to measure the volume of the remaining gas. Lavoisier used mercury to absorb the oxygen. Moist iron filings, phosphorus, or a mixture of potassium hydroxide and pyrogallic acid can also be used effectively.

For more than two hundred years air had been studied and analysed with more attention than any other substance, and by the most gifted chemists. Its composition was already considered settled, when in 1895 Lord Rayleigh and Sir William Ramsay startled the scientific world by announcing to the British Association that they had found a new gas in the air. The statement was at first scarcely believed, but the evidence was so convincing that the statement could not be denied. Rayleigh had found that the nitrogen prepared from air by extracting the oxygen was heavier than the nitrogen prepared from other substances. Ramsay found that if atmospheric nitrogen were passed over hot magnesium, most of the nitrogen united with the magnesium. But there was a part which, no matter how frequently it was passed over the heated magnesium, remained inert, and could not be made to unite with it. This he recognized as a new component of the air and called it *argon*. Hence atmospheric nitrogen is really a mixture of nitrogen and argon; and as the latter is heavier than nitrogen, atmospheric nitrogen is heavier than pure nitrogen formed in other ways. Since that time Sir William Ramsay has found no fewer than five other components in the air: namely, *helium*, *neon*, *krypton*, *xenon*, and *niton*. While argon forms almost one per cent. of the air, these form only an infinitesimal part of it.

In addition to these components air contains variable quantities of water vapour, carbon dioxide, ammonia, and other gases.

When these latter substances are taken from the air, the percentage of the main components is almost invariable. Whether the air be taken from over the ocean, from the top of a mountain, or from the depths of a mine, it contains approximately the same percentage of oxygen and nitrogen. However, by very accurate experiments, differences in composition are noted, and these differences are too great to be accounted for by any errors of experiment. Moreover, meteorologists state that in the higher strata of the atmosphere the percentage composition differs very greatly from its composition in the lower strata.

24. Properties.—One litre of air at 0°C. and 760 mm. pressure weighs 1.293 grams.

When air is dissolved in water, the proportion of oxygen to nitrogen is changed. The following table shows this plainly:

	Air dissolved in water	Air undissolved in water
Oxygen..........	35.1	20.96
Nitrogen.........	64.9	79.04
	100.0	100.00

25. Liquid air.—It seems strange to think of air in a liquid or solid state. Yet under great pressure and at a very low temperature the air turns into a transparent liquid of a faint blue colour, and if the temperature is lowered still more, the air becomes jelly-like and finally turns to a white solid with a tinge of blue in it.

Liquid air is prepared in a complicated apparatus, the construction of which is made clear by Figure 9. N is a compression pump that can utilize either the air as it returns from the liquefier, or external air which is admitted at A by the opening of a valve. In the coils in L the air is compressed and cooled by the cold water which circulates through the outer vessel. The spiral coil in H is composed of a double set of pipes, one inside the other, and the length of pipe is very great in the real machine. The compressed air passes in through the inner pipe and escapes through the nozzle (M) into the tank (F); here it suddenly expands as the pressure is diminished, and like all expanding gases it becomes cooled. It then passes back through the outer pipe (E), and, as it does so, it cools the compressed gas which is passing in the opposite direction in the inner pipe. As the air is kept in continuous circulation, it becomes cooler and cooler until it reaches about—190°C., when some of it condenses into a liquid in the reservoir (F). By continually allowing new air to enter at A more liquid accumulates at F., and can be drawn off through the tap (T). It is usually kept in Dewar flasks (Fig. 10). These are made of double metal, and have a vacuum in the space between the two layers of metal. Liquid air can be kept for many hours in such vessels, plugged with cotton wool. If liquid air is left in an open vessel, it becomes richer in oxygen, because the nitrogen evaporates at a lower temperature than the oxygen, and on account of this phenomenon it is possible to obtain pure oxygen and pure nitrogen from liquid air. Immense quantities of these gases are now prepared in this way; the oxygen is used for oxy-acetylene welding and for metal cutting, while the nitrogen is used for preparing cyanamide (Sec. 22).

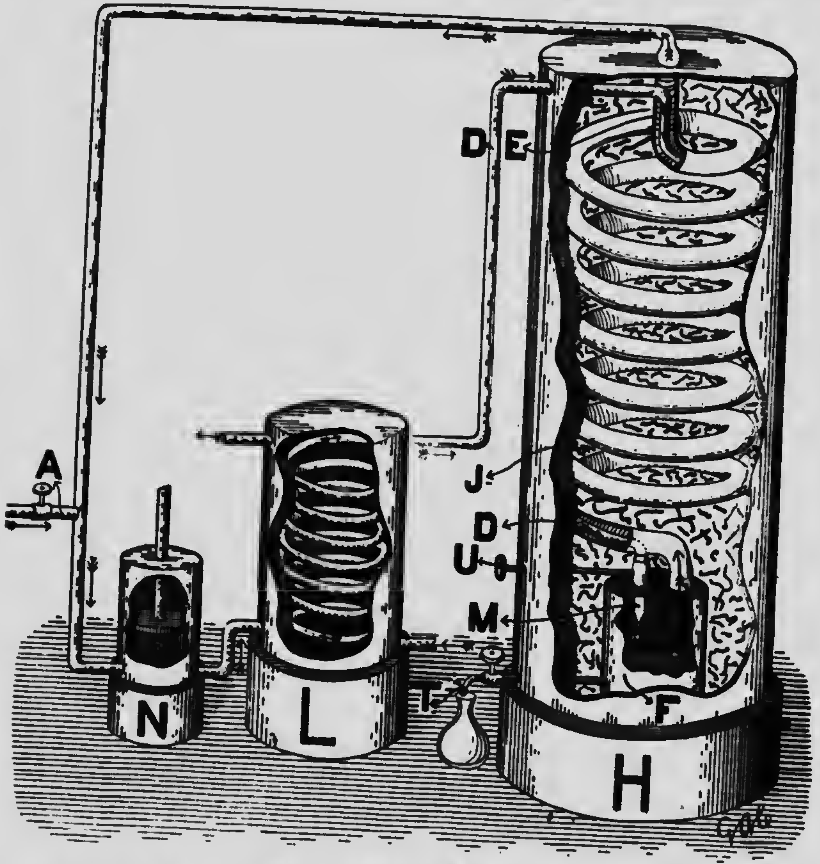

FIG. 9.—LIQUID AIR MACHINE

A. Tap admitting air to the machine. D. Tube containing air under high pressure. E, Outer tube containing air under low pressure. F. Tank containing liquid air. H. Machine in which the liquid air is produced. J. Outer vessel containing the coiled tubes; these latter are surrounded by non-conducting material. L. Coils surrounded by running water. M. Nozzle through which the air under pressure expands. N. Air-pump. T. Tap for drawing off liquid air. U. Valve to regulate the expansion of compressed air.

As the uses of these gases are bound to increase, their preparation will become of increasing importance. Already commercial plants for this purpose are in operation at Toronto and Montreal.

Liquid air produces a remarkable effect on substances by lowering their temperature. If a rubber ball were immersed in liquid air and then taken out and thrown on the floor, it would fly to pieces like a ball of glass; on the other hand, a ball of iron, if thrown on the floor after immersion would rebound almost like rubber. A tin cup containing liquid air becomes as brittle as glass. If a jet of burning gas is plunged into liquid air it continues to burn, while the water formed by the burning turns into ice.

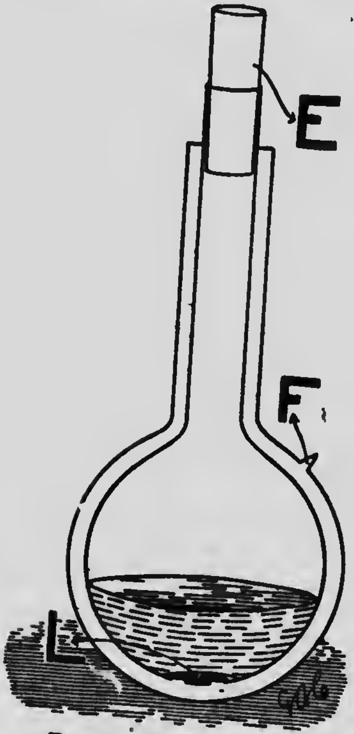

FIG. 10.—DEWAR'S FLASK

E. Stopper made of hollow exhausted glass cylinder. F. Point where vessel was sealed off after exhaustion. L. Pocket containing charcoal which absorbs last trace of gas.

QUESTIONS

1. How can it be proved experimentally that air is composed of oxygen and nitrogen?

2. What is a catalyst? What facts do we require to prove regarding a substance, to be sure it is a catalyst?

3. How would you explain the tarnishing of metals in the air? What metals do not tarnish? Why?

4. In tinware the vessels are made of sheet-iron covered with tin. Why is the iron so covered?

5. A 1,000 c.c. flask is filled with tap water at 10°C. The water is boiled and the dissolved gases occupying 22.37 c.c. are collected in a gas bottle over mercury. Some moist iron filings are inserted into this gas and the volume gradually shrinks to 14.50 c.c. Find how many cubic centimetres of oxygen and of nitrogen are dissolved in 100 c.c. of water. (Assume that only nitrogen and oxygen are dissolved in water.)

6. A quantity of air is passed over heated copper in a combustion

tube, and the nitrogen that passes over is collected in an evacuated globe.

The empty globe weighs........................391.534 grams.
The globe+nitrogen weighs........................403.907 grams.
The combustion tube before the experiment weighs.....647.666 grams.
The combustion tube after the experiment weighs.....651.348 grams.

Find from these data how many grams of nitrogen and how many of oxygen are contained in 100 grams of air.

7. If the air were pure oxygen, how would it affect the burning of substances?

8. Is oxygen a suitable gas with which to fill balloons? Give reasons for your answer.

9. Describe four methods by which oxygen may be removed from the air.

10. Why is oxygen not used instead of air for the draught in furnaces and stoves?

11. A mixture of equal volumes of oxygen and nitrogen is shaken up thoroughly in a bottle with water which has been recently boiled. In what respect is the composition of the gas which remains in the bottle above the water changed? How would you show this difference by experiment? If the water were boiled, and the gas that came off from it collected, in what respect would its composition differ from that of the original mixture?

12. Calculate the weight of one litre of a mixture of oxygen and nitrogen in equal volumes. (There is no change in volume on mixing.)

13. If 21 litres of oxygen are mixed with 79 litres of nitrogen to make 100 litres of the mixture, all measured at 0°C. and 760 mm. pressure, find the weight of one litre of the mixture. Compare it with the weight of one litre of air (Sec. 24).

CHAPTER III

SOME CHEMICAL LAWS AND TECHNICAL TERMS

> "Substances were thought of as things distinct from their qualities; as things whose real nature was concealed by their envelopes and did not become apparent until these envelopes, which were the qualities of the substances, had been destroyed."
>
> — *Pattison Muir*

26. Pure substances.—Now that we have studied several substances, have learned how they react, and have obtained a little insight into the method of conducting an investigation, we had better pause to give more exact significance to some of the words we have been using, and to classify some of the facts which we have learned.

We consider the world to be composed of bodies, each of which has a definite form and size. But many of these bodies we recognize as composed of the same substance. A chair, a table, and a door are different bodies, but each is composed of the same substance, wood. We have applied names to many of these substances, such as iron, granite, air, and water. If substances are more closely examined, it is found that they can be divided into two great groups. If specimens of water from the sea, from a lake, from a turbid stream, and from a rain barrel are examined, it is found that they differ very greatly in their colour, taste, specific gravity, boiling-point, etc. If each is boiled and the vapour that passes off is condensed, the liquid obtained in each case is identical in its colour, taste, boiling-point, specific gravity, and in many other respects.

This liquid we call pure water, and though it can be prepared by many methods, it always has identical properties. The substance, silver, can be prepared in a variety of ways and from many substances, but it is possible in every case by purification to obtain a substance with identical properties; this substance is called pure silver. Substances like pure water and pure silver that, though prepared by a variety of processes, have identical properties are called *pure substances.*

27. Properties of pure substances.—Compare a silver medal, a silver spoon, and a silver thimble. Each is a separate body. They differ from each other in several respects; they have different weights, different volumes, and different shapes; they feel different to the touch, the spoon feeling smooth, the thimble rough; one may feel cold, another warm, etc. But they have also many properties in common. All have the same colour and lustre; the specific gravity is the same for all; all fuse at 960°C.; all boil at a white heat; all conduct heat and electricity, etc. Again, if they are dropped into nitric acid, all are destroyed and brown fumes are given off; while if they are heated with sulphur, all turn black. The differences are accidental, and it is possible to change any one of the accidental properties with ease, and leave the other properties unchanged. The ways in which they resemble each other are, however, fundamental, and no fundamental property can be changed without changing them all.

The fundamental properties possessed by all bodies composed of silver are called *specific properties;* the incidental properties such as shape, volume, weight, etc., are called *attributes;* while the temperature, pressure, or electrical state that affects these specific properties is called a *condition* of the body. Similarly every pure substance can be moulded into many bodies. In this respect we may compare bodies with individual animals or plants. Certain individual animals have some characters in common, and all those animals which have these common characters are said to belong to the same species. The qualities they have in common are called the *specific* characters. Similarly a pure substance is sometimes called a *chemical species*, and, as we have just said, the characters common to the different bodies composed of this substance are called the specific properties. In one important respect the pure substance differs from the animal species. In the animal kingdom the individuals show slight differences even in the specific characters. In the pure substances, however, there is absolutely no variation. Each specimen has always exactly the same specific properties, and if any of these properties change in the least, the specimen is no longer held to be the same pure substance.

This fact that a pure substance always possesses the same properties is the fundamental law of chemistry, and is called the *law of the conservation of properties*. Chemists were very slow to realize the truth of this law, and yet the chief work of chemistry (finding the properties of substances) would be a useless task, if these properties were not fixed, but varied from day to day or differed in different localities. Silver, wherever it is found or however it is produced, always possesses the properties already stated.

It is to be observed that the specific properties of a pure substance are dependent on its conditions of temperature, pressure, etc. The colour of silver is white and metallic at a low temperature only, while at a higher temperature it changes to a luminous red. So, to be strictly accurate, when the specific properties of a pure substance are stated, the conditions under which it possesses these properties should also be indicated.

In identifying a body it is not necessary, in practice, to find whether it possesses all the specific properties of its species; but if it is found to possess two or three of them, it is almost certain to possess them all. If a body were tested and found to melt at 960°C. and to turn black when heated with sulphur, these facts would be sufficient to identify it as silver.

28. Mechanical mixtures and solutions.—Many substances are not like pure water and pure silver. If a number of salt solutions are examined, it is found that the different members have not identical properties, but differ in taste, specific gravity, boiling-point, and in other specific properties, and all the possible salt solutions can be arranged in a set with each property changing steadily as we pass along the set. In a single member of the set the properties are uniform throughout the mass; in other words it is *homogeneous*. Such mixtures are called *solutions*, and their properties will be more fully studied later. Air is a solution of oxygen and nitrogen, and many alloys are solutions of two or more metals.

If several specimens of muddy water are examined, it is found that the various specimens, like the solutions, differ in some of their properties, such as colour, taste, and specific gravity; but unlike the solutions the boiling-point, freezing-point, vapour pressure, etc., are the same in all the specimens, and in every case are identical with those of the water, indicating that the properties of the water remain unchanged. Moreover, a sample of the liquid is not homogeneous, as the solid particles can be detected by the cloudiness. A substance showing such properties is called a *mechanical mixture*. Granite, smoke, soil, and many other substances, are mechanical mixtures.

All solutions and mechanical mixtures can be made by mixing together pure substances, and the word *mixture* is used in this book to include both.

Thus all substances can be classified according to the following scheme:

- Substances
  - pure substances
  - mixtures
    - solutions
    - mechanical mixtures

29. Physical and chemical change.—If a piece of iron is filed until it is entirely converted into iron filings, a marked change has taken place in it, but each particle has the same specific properties as the original piece; that is, has a bright metallic appearance, is attracted by a magnet, melts at the same temperature, etc., and hence is the same pure substance. But if we allow the iron filings to remain in a damp atmosphere for a few days, a remarkable change takes place. Iron rust replaces the iron, and we have a pure substance with entirely different specific properties; in other words we have a different pure substance. Similarly, when red mercury oxide is heated, this pure substance disappears, and two other pure substances, oxygen and mercury, are formed, which are quite unlike the red oxide in their properties. Changes like the rusting of iron, the heating of mercury oxide, or the burning of magnesium, in which one or more new pure substances are formed, are called *chemical changes;* changes in form, size, temperature, pressure, magnetic conditions, etc., are called *physical changes.* While the foregoing characteristics will usually allow one easily to decide to which class any change belongs, there are certain phenomena, such as melting and boiling and the process of solution, that are sometimes placed under physical change and sometimes under chemical change. The more usual practice among chemists, however, is to call them physical changes. Whenever any substance or substances undergo a chemical change in the laboratory, such a process is called a *chemical reaction.*

30. Physical and chemical properties.—Substances have two kinds of properties. Silver is a white, lustrous, ductile metal; its specific gravity is 10.5; it conducts heat and electricity well. These properties do not involve the changing of silver into another pure substance, and such properties are called *physical properties.* Silver, when acted on by nitric acid, forms a white salt; and, when it is heated with sulphur, it is converted into a black substance. These properties involve the conversion of silver into some other pure substance, and such properties are called *chemical properties.*

31. Conservation of weight.—Many phenomena might lead one to think that substances can be entirely destroyed. A candle burns away and seems to leave nothing behind. A pound of coal when consumed leaves only a few ounces of ashes. On the other hand substances might sometimes appear to be created out of almost nothing. Three centuries ago van Helmont, a Belgian scientist, planted a willow tree weighing 5 pounds in a pot of earth, which when dry weighed 200 pounds. He added nothing to the pot but pure water, yet at the end of five years the willow weighed 169 pounds. When the pot of earth was dried the surprising result was found that it had lost only two ounces in weight. Where had the added 164 pounds come from? If, however, these examples are examined, the results may be easily accounted for. Though the candle and the coal disappeared, it is easy to prove that gases and smoke passed off from them, and that these have weight. While the willow increased in weight by 164 pounds and absorbed only a few ounces from the earth, yet the increased weight may have been absorbed from the water or the air, for it is well known that much plant food is obtained from these sources. Evidently only the most exact experiments can settle the question whether substances ever entirely lose any of their weight in being transformed into other substances.

Lavoisier was the chemist who first devoted serious attention to this problem. He placed tin in a large glass vessel, sealed up its neck, and weighed the whole. The tin was then heated until it melted, and was kept at that temperature for several hours, until part of the tin was converted into a blackish powder. The whole was weighed again, and it was found that there was neither loss nor gain of weight. He performed many similar experiments, and always obtained the same results. He was thus able to establish the great chemical *law of the conservation of weight*, namely, that *in any chemical reaction the total weight of the reacting substances is the same after the reaction as before it.* The law can be easily illustrated in the laboratory.

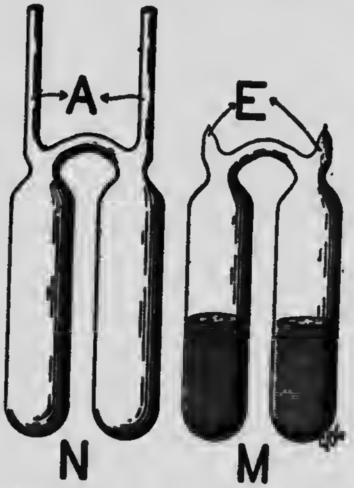

Fig. 11.—Landolt's Tube for Proving Conservation of Weight
N. Tube ready for filling.
M. Tube filled and sealed off.
A. Tubes for filling.
E. Points where the tubes were sealed off.

Into a flask containing 10 c.c. of silver nitrate solution insert a test-tube half filled with a solution of common salt. Cork the flask and weigh it accurately; then tilt it up so that the salt solution runs out into the flask. A chemical change at once occurs, a curdy, white precipitate being formed. Then weigh the flask and contents again, and it will be found that no loss or gain of weight has occurred, though a new substance has been formed.

This law has been re-investigated recently by Landolt, who used a tube like Figure 11. In the two arms he placed substances that reacted on each other. Then the tube was sealed off at the top and weighed with great precision. The liquids were mixed by tilting the tube, and the apparatus was weighed again. He found after conducting such experiments for twenty years with various sets of substances, that if there is any change at all in weight during a reaction, it is less than one part in ten million.

This law has been assumed in some of the experiments discussed in preceding chapters. Magnesium when heated in air increases in weight, and we inferred from this that it had absorbed a part of the air. If substances were liable to gain or lose weight without either uniting with any new substance or giving any off, no inferences could be made, because a substance might change its weight at any time. But this law teaches that every substance carries its weight with it through all its reactions.

32. Elements and compounds.—If mercury oxide is heated strongly, two pure substances are produced, and the sum of their weights is equal to the weight of the oxide used. Similarly, if potassium chlorate is heated, two pure substances are produced from it whose combined weight equals the weight of the potassium chlorate. In the case of the mercury oxide the two substances produced are oxygen and mercury; and in the case of the potassium chlorate, oxygen and potassium chloride. It is possible to obtain from potassium chloride two substances called potassium and chlorine, whose combined weight is exactly equal to the weight of the potassium chloride from which they were obtained. Oxygen, mercury, potassium, and chlorine have been subjected to many chemical operations, but never has any one of them been decomposed into two or more pure substances. Pure substances like mercury oxide, potassium chlorate, and potassium chloride are called *chemical compounds*, or more briefly, compounds; while substances like oxygen, mercury, potassium, and chlorine, which have never been decomposed, are called *elements.* Accordingly, all pure substances are divided into these two classes.

As mechanical mixtures and solutions can be prepared by mixing pure substances, they also can be decomposed into elements. Most of the many thousands of pure substances that can be prepared are chemical compounds, only about eighty of them being elements. All of these compounds are formed by the combination of two or more of these elements in various proportions.

From what has been stated regarding elements, it will be inferred that some substances which are now considered elements may in the future be decomposed; they will then be classified as compounds. Such has been the fate of some of the substances formerly classed as elements, and there can be little doubt that future investigation will show that others also are compounds.

33. Conservation of elements.—One element cannot be converted into another element, and if two elements unite to form a compound, none but these two elements can ever be obtained from that compound. Elements, then, may pass in and out of compounds, but they are always conserved. This general fact of the permanence of the elements is frequently called the *law of the conservation of the elements.* For hundreds of years the whole energy of chemists, or alchemists as they were called, was devoted to the converting of one element into another. They were particularly interested in endeavouring to convert the baser metals, such as lead, into silver or gold, but, of course, they failed. It was only after hundreds of years of failure, that this law of the conservation of the elements was established. Within the last few years, however, one of the most brilliant chemists, Sir William Ramsay, revived the doctrine of the transmutation of the elements; as some careful work of his would seem to indicate that the law of the conservation of the elements is not true in all cases, and that, in some cases at least, one element may be converted into another.

34. Combination and decomposition.—When two pure substances unite chemically to form a single new pure substance, as when magnesium burns in oxygen to form magnesium oxide, the chemical reaction is called *combination*. When one pure substance is decomposed to form two or more pure substances, as when mercury oxide produces mercury and oxygen, the chemical reaction is called *decomposition*. Other examples of combination are the burning of iron, charcoal, and sulphur in oxygen, when these unite with oxygen to form iron oxide, carbon dioxide, and sulphur dioxide, respectively. Other examples of decomposition are the heating of potassium chlorate to form oxygen and potassium chloride; and the heating of manganese dioxide, potassium permanganate, and barium dioxide to produce oxygen, the other product of the decomposition in each case being left as a residue in the test-tube.

35. Law of definite proportions.—If some mercury oxide is weighed and then heated in a hard-glass test-tube until all the oxygen is given off, and if the residue of mercury is then weighed, the percentage composition can be readily found. The data furnished by such an experiment are as follows:

Weight of test-tube	120.232 grams.
Weight of test-tube+mercury oxide	121.332 grams.
Weight of test-tube+mercury	121.250 grams.

The weight of mercury oxide is 121.332−120.232= 1.100 grams.
The weight of mercury is 121.250−120.232= 1.018 grams.
As 1.100 g. of oxide contains 1.018 g. mercury and .082 g. oxygen.

$$\therefore\ 100\text{ g.}\quad \text{“}\quad \text{“}\quad 1.018\times\frac{.100}{1.100}\text{ g.}\quad \text{“}\quad \text{“}\quad .082\times\frac{.100}{1.100}\text{ g.}\quad \text{“}$$

$$\text{or } 92.54\,\%\quad \text{“}\quad \text{“}\quad \text{“}\qquad 7.46\,\%\quad \text{“}$$

If all the members of a class were to perform this experiment carefully from different samples of mercury oxide, each would find approximately the same percentage composition; and if a number of trained chemists were to repeat the experiment, the results would agree still more closely. Mercury oxide can be prepared in various ways, but no matter how it is prepared the percentage composition is found to be exactly the same. The same result is obtained in the examination of the composition of all pure substances. Hence we are able to draw the conclusion that *if all samples of a compound substance are examined, the proportion by weight of the elements that compose it is always the same.* This general fact is called the *law of definite proportions* or the *law of constant composition.* The proportion of magnesium to oxygen in magnesium oxide is 60.4 grams of magnesium to 39.6 grams of oxygen. If, therefore, magnesium reacts with oxygen to form magnesium oxide, these elements must be present in this proportion in order that the reaction may be complete. If 60.4 grams of magnesium is burned it will combine with 39.6 grams of oxygen. If there is more than 39.6 grams of oxygen present, the extra amount will be left unused, and if there is less than 39.6 grams of oxygen present, some of the magnesium will remain unburnt. This relation between the percentage composition of a pure substance and the proportion in which its constituents react to form it obtains in all chemical reactions, and follows directly from the law of definite proportions. In fact the law is sometimes stated in this form: *The proportion in which pure substances react is fixed.* This law should never be forgotten by pupils when performing experiments. If in a test-tube there are only a few drops of a substance to be reacted on, it is usually useless and wasteful to add a large quantity of a reagent to react with it.

36. Compounds and mixtures. — Compounds and mixtures resemble each other insomuch as both can be decomposed into two or more pure substances; but they have also marked differences. All compounds have their constituents in a fixed proportion. It is quite otherwise with mixtures. If various samples of air are analysed, the proportions of oxygen to nitrogen vary slightly. If a number of salt solutions prepared in various ways are examined, the proportions of salt to water will vary widely. If various gunpowders are examined, the proportions of saltpetre, sulphur, and charcoal will be found to vary considerably. Air, brine, and gunpowder are mixtures, and to these the law of definite proportions is not applicable. In fact, it would be correct to define a chemical compound as one that has its constituents in a definite proportion in all samples, and to define a mixture as a substance that has its components in varying proportions in different samples. The pure substances into which a compound can be separated are called its *constituents*, while the substances into which a mixture can be separated are called its *components*.

In this chapter an effort has been made to classify bodies and phenomena from the chemical standpoint. Let it be understood, however, that though it is convenient and necessary to classify the objects of nature by drawing a line somewhere which will separate them into groups, there are, nevertheless, no hard and fast lines in nature. There will always be objects and phenomena about which it will be difficult to decide in which group they should be placed, because in nature there is a gradual transition in passing from one end of the series to the other. These doubtful cases will generally be ignored in this elementary text-book, so as not to confuse the beginner.

Having investigated the composition and properties of air and its components, and having classified the reactions and bodies met with in the investigation, we shall next undertake a similar investigation of the commonest of all liquids, water. Having shown that it is a pure substance and not a mixture, the question rises whether it is an element or a compound. If it proves to be a compound, it will be of great interest to find the elements that enter into its composition and to learn their properties.

QUESTIONS

1. State the chief differences between mixtures and compounds, and between solutions and mechanical mixtures.

2. If iron filings and sulphur are ground together to make a fine powder, how would you test to find if the fine powder is a mechanical mixture or a compound?

3. What is meant by a homogeneous body? How would you prove experimentally whether a sample of water is homogeneous or heterogeneous? Name five homogeneous substances or mixtures, and five heterogeneous mixtures.

4. Supposing you were asked to find experimentally whether sugar is an element or compound, how would you proceed?

5. Classify the following as physical change or chemical change, giving reasons in each case: (*a*) a piece of iron rusts; (*b*) a piece of iron is magnetized; (*c*) a piece of rubber is stretched; (*d*) milk turns sour; (*e*) a match burns; (*f*) a piece of cloth shrinks; (*g*) a piece of brass tarnishes; (*h*) a wax candle burns.

6. Make a list of all the specific properties mentioned in this chapter. Add any others you know of.

7. A porcelain boat weighs 22.361 grams. Some copper filings are put into it, and it then weighs 23.361 grams. The porcelain boat is placed in a combustion tube, and the latter is heated strongly. Oxygen is passed through the combustion tube until all the copper is converted into copper oxide; the boat with contents now weighs 23.612 grams. From these data calculate the percentage composition of copper oxide.

8. A hard-glass test-tube weighs 110.56 grams. When a quantity of potassium chlorate is added, the two together weigh 111.79 grams.

The test-tube is then heated until all the oxygen is driven off, and the test-tube and its contents (potassium chloride) now weigh 111.31 grams. Calculate the percentage of oxygen and of potassium chloride in potassium chlorate.

9. When distilled water is boiled in a glass vessel for a long time, an earthy deposit forms in the water. It was believed that part of the water was converted into earth. To find the origin of the earth, Lavoisier took a flask which weighed 11338.62 grains, and added rain-water, seven times distilled, until the combined weight was 38463.62 grains. He then kept the water at 80°C. for 101 days. The two then weighed 38463.87 grains. The empty flask weighed 11321.22 grains, and when the water in the flask was evaporated, the residue weighed about 20 grains. Taking into consideration the errors of experiment, what does this experiment indicate to be the probable source of the earthy deposit?

CHAPTER IV

WATER AND HYDROGEN

WATER

> "By the experiment with the globe, it appeared that when inflammable (hydrogen) and common air are exploded in a proper proportion, almost all the inflammable air, and near one fifth of the common air, lose their elasticity, and are condensed into dew, and by this experiment it appears that this dew is plain water, and consequently that almost all the inflammable air, and about one fifth of the common air, are turned into pure water."
>
> —*Henry Cavendish, 1784*

37. History.—From the very earliest times water was considered to be an element. Thales, a scholar at the very dawn of Greek history, believed that water was the one element from which all other substances were derived. Aristotle placed it among his four elements, the other three being air, fire, and earth, and there it remained for many centuries. The Honourable Henry Cavendish first clearly proved the real nature of water in the set of experiments whose conclusion is recorded in the quotation at the head of this chapter.

38. Physical properties of water.—Water is a colourless liquid which is taken as the standard for estimating specific gravity, so that its specific gravity is 1. It was also selected at first as the standard for estimating mass, for the mass of 1 c.c. of water at 4°C. was called 1 gram. It freezes at 0°C. and boils at 100°C. It is the best solvent we know of, and the one most frequently used for making solutions. Many pure substances which do not react when brought into contact, react vigorously when their aqueous solutions are mixed. Water dissolves all gases to a certain extent. Some, such as ammonia, dissolve in it in very large quantities, while others, such as oxygen and nitrogen, dissolve only to a slight extent. Yet, as we have already seen, the oxygen dissolved from the air plays an important role in the economy of nature. All the varied plants and animals of ocean and river, lake and pond, are dependent upon it for the means of respiration, and could not live in the water if the latter ceased to dissolve oxygen. The dissolved oxygen serves another equally important function. When we consider the vast quantities of sewage, decaying plants and animals, and other filth, which are swept into the rivers and seas, it is easy to realize how soon their waters might become foul and polluted, if the dissolved oxygen did not act on these impurities and convert them rapidly into harmless substances which are not repugnant to the palate or the nostrils.

39. Natural waters.—Absolutely pure water is very difficult to prepare and is never found in nature, for as soon as water comes in contact with air or earth, it begins dissolving substances from it. Natural waters may be appropriately classified into (1) rain-water, (2) surface-water, (3) sea-water, and (4) spring-water.

(1) *Rain-water* is the purest of the natural waters, as it is formed by the condensation of the water vapour in the air. While dropping through the atmosphere it dissolves, it is true, oxygen, nitrogen, and salts of ammonia, and it also has dust particles mixed with it; but as it has not been in contact with the earth, it contains none of the latter's soluble components. It is excellent for use in the laboratory when distilled water is not available.

(2) *Surface-water.* This includes the water found in rivers and lakes, that has flowed over the surface of the

earth and has had an opportunity to dissolve any soluble materials contained in the soil. It usually has a considerable amount of dissolved mineral substances, and also some organic matter, the product of decaying plants or animals. Besides the dissolved matter, it contains a certain number of solid particles which make it more or less turbid.

(3) *Sea-water* contains very much larger quantities of dissolved salts than any of the other kinds. Common salt forms a large proportion of these dissolved salts. This gives sea-water a markedly saline taste and makes it quite unfit to drink.

(4) *Spring-water* originates from surface-water that has penetrated into the rocks, and has quantities of their soluble components dissolved in it. If the water has come from great depths or has passed near heated lavas, it may be still warm when it comes to the surface, and it usually has large quantities of salts dissolved in it, as the salts are more soluble in hot than in cold water. These so-called mineral waters are said to have curative values for various diseases, according to the salts they contain. They are found in several places in Canada, among others, at St. Catharines in Ontario, and at Banff in Alberta.

40. Tests for water.—Pupils will be constantly producing clear liquids in the experimental work of chemistry and will require to know whether these liquids are water or not. It is, therefore, necessary to state some tests by which water even in small quantities can be detected: If it is present in a large quantity, the freezing-point and boiling-point will be sure tests. If a drop of water is put on a lump of anhydrous copper sulphate, the latter at once turns blue. If a little particle of sodium is placed in a drop of water, a gas is generated and the sodium becomes warm. These two tests will readily detect water even in the smallest quantity. The taste also furnishes an easy test.

41. Action of metals on water.—In our investigation of the composition of air, we began by considering the effect of heating in it certain metals and other elements. A similar method may be tried with water. Indeed, metals can be divided into classes, according to the manner in which they behave towards water.

Some react on water as soon as they touch it. Sodium floats about on the surface and becomes so hot that it is converted into a molten globule, which hisses about on the surface and gradually disappears. When the liquid which remains is examined, it is found to be quite different in its properties from the original water. It feels slimy, tastes like soap, turns red litmus blue, and when evaporated leaves a white solid behind.

Calcium reacts on water also, but sinks to the bottom, and bubbles of gas arise from the calcium, which itself becomes smaller and smaller, and finally disappears. When the liquid which remains is examined, it is found to have similar properties to those which the water had after the sodium had acted upon it. As calcium is an element, the gas probably came from the water, unless it was formed by the union of the calcium with a part of the water. Other metals like magnesium do not react with water at ordinary temperatures; but if the temperature of the water is raised to the boiling-point, then the magnesium acts slowly on the water, and a gas is given off. If the magnesium is first heated with a drop of mercury, the action is quite vigorous, though the mercury is left unchanged in properties and quantity, and acts only as a catalyst. Other metals, such as iron and zinc, show no action even when the water is boiling.

To provide conditions similar to those in which metals were heated in air, the water should be in the gaseous state, and the metals should be heated to a high temperature in the steam. When this is done, iron and zinc also act upon the steam, and magnesium acts with great intensity.

Lavoisier was the first to use this method, using iron for the purpose. Figure 12 shows the original apparatus that he used. A gun barrel (E F) was placed in the charcoal furnace, and was connected with a vessel (A) containing water, and this water was allowed to flow drop by drop into the red-hot gun barrel. The spiral worm (S) condensed any undecomposed steam. The hydrogen which passed on was collected over water. The oxygen of the water united with the iron of the gun barrel.

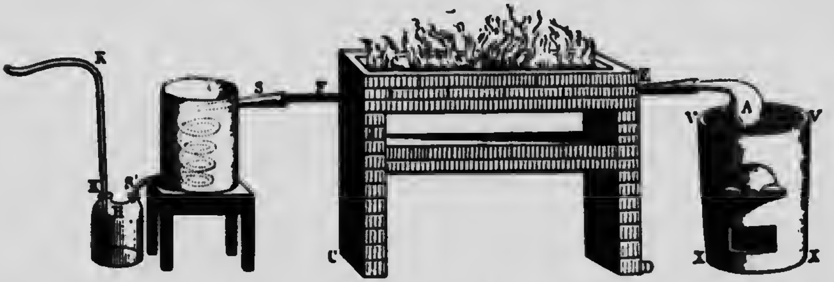

FIG. 12.—LAVOISIER'S ORIGINAL DRAWING OF APPARATUS BY WHICH HE PROVED WATER CONTAINS HYDROGEN

A. Retort containing water being boiled over charcoal furnace, V. F. Gun-barrel made red hot in charcoal furnace, C D. S. A spiral coil in which undecomposed steam was condensed, and from which it runs into H. K. Tube through which hydrogen passes.

Perhaps the simplest way to show this action is to plunge a lighted magnesium ribbon into a flask in which water has been boiling long enough to drive out all of the air. The magnesium ribbon continues to burn, and when the ash is examined, it is found to be identical in its properties with the ash which is formed when magnesium is burned in oxygen. Both are white, both dissolve very slightly in water, and their solutions turn red litmus blue.

42. Qualitative composition of water.—From the identity of properties in the two substances just dealt with, a very important conclusion can be drawn regarding the composition of water The ash is magnesium oxide and is composed of magnesium and oxygen, as we have already proved. The oxygen must have come from the water, of which, accordingly, it is a constituent. By modifying the experiment, it is possible to find another constituent. We have already learned that a gas is formed when the metals, iron, zinc, and magnesium, act on the water, and it will be necessary now to arrange our apparatus so that when the magnesium burns in the steam, any gas formed may be collected. Figure 13 shows a simple method of accomplishing this: The water is boiled in the flask (E). The connecting tubes are as short as possible, and when steam is passing through them, the magnesium in the combustion tube (F) is gradually heated until all the condensed vapour is driven out. Then the

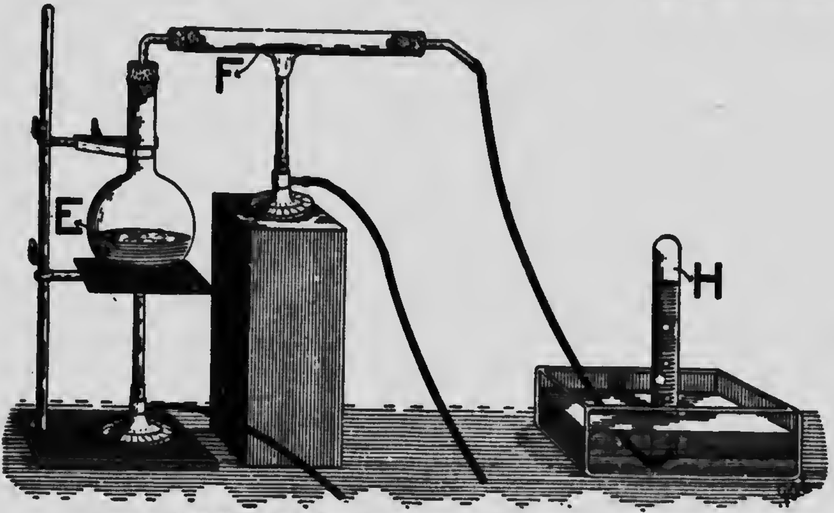

FIG. 13.—APPARATUS FOR DECOMPOSING WATER BY PASSING STEAM OVER HEATED MAGNESIUM
E. Water. F. Magnesium. H. Hydrogen.

magnesium is heated intensely, until finally it ignites in the steam and burns vigorously, giving off a gas which collects in the test-tube (H). When this test-tube is raised from the water with the mouth held downward, and a burning splint is applied to it, the gas burns at the mouth of the tube. We have thus a new gas quite different from either oxygen or nitrogen. Is this new gas a constituent of the water? It looks probable, but it will be necessary first to prove that it is not formed by a part of the magnesium combining with a part of the water.

The ratio of the weight of the magnesium ribbon to the weight of the magnesium oxide formed will be found to be the same whether the metal is burned in steam or air. In this case, therefore, all the magnesium used is contained in the magnesium oxide. As magnesium oxide always has the same percentage composition, all of the magnesium burned in the steam must have gone to form the magnesium oxide, and none went into the gas. This combustible gas, which is called *hydrogen* and which is an element, is, therefore, really a constituent of the water. We thus reach the conclusion, as did Cavendish almost a hundred and fifty years ago, that water is not an element but a compound, and has for its constituents the two gaseous elements, oxygen and hydrogen.

43. Quantitative composition of water.—So far we have confined our attention to a *qualitative analysis* of water, that is, we have merely found the constituents of which it is composed. It will be necessary now to make a *quantitative analysis* and find in what proportions the constituents are present.

The simplest method of showing the proportions by volume in which the gases unite to form water, is by means of a eudiometer. Of this apparatus there are various forms, the simplest of which is a thick cylindrical glass tube (Fig. 14) closed at one end and graduated in cubic centimetres. The closed end has two platinum wires sealed through it, and the ends of these wires within the eudiometer are separated by a space of one millimetre. This tube is filled with mercury or water and inverted over the same liquid. Hydrogen is passed into it (say 10 c.c.), then oxygen is passed in until the total volume of gases is 21 c.c. The secondary of an induction coil is connected with the platinum terminals, and a spark causes the gases to ignite. The volume of gas diminishes to 6 c.c., and when this is tested it proves to be oxygen. Accordingly, neglecting the volume of the water, which is in the liquid state, we conclude that 10 c.c. of hydrogen unite with 5 c.c. of oxygen to form water. Cavendish repeated this experiment many times and found that these two gases unite invariably in the proportion of two to one. As in this experiment the composition of water has been found by actually combining the two gases to form the water, this method is called *synthesis*.

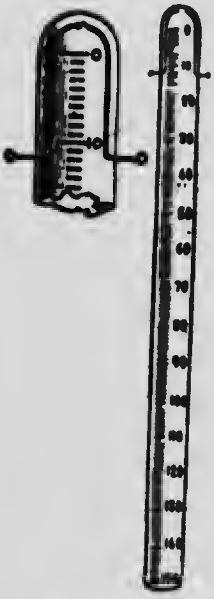

FIG. 14.—EUDIOMETER At the left is the upper end showing the platinum terminals.

The proportions by volume can be found by *analysis*, that is, by decomposing water into its constituents. Figure 15 illustrates a simple form of apparatus for this process. A wide-mouthed bottle (F) has the bottom half cut off. A cork is inserted, through which two gas carbons (H) project about two inches. Melted paraffin (L) is poured on the cork after it has been inserted in the bottle, to make it water-tight. Water is poured into the inverted bottle until the carbons are well covered, and a few drops of sulphuric acid are then added. Two long test-tubes are filled with the same liquid and inverted over the carbons. The terminals of a battery of several cells are attached to the parts of the carbons which project below. Bubbles of gas appear at each terminal, and the volume at one terminal (E) is about twice as great as the volume at the other (N). If the larger volume is tested with a burning match, it proves to be hydrogen, and the smaller volume proves to be oxygen. It might be thought that the sulphuric

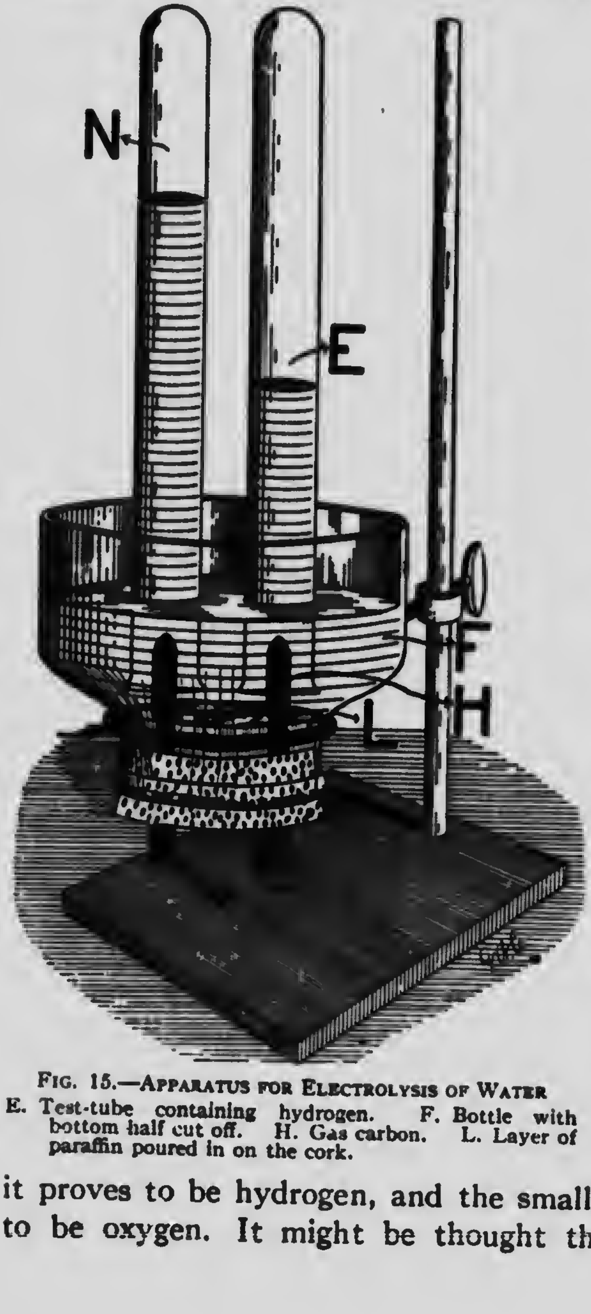

Fig. 15.—Apparatus for Electrolysis of Water
E. Test-tube containing hydrogen. F. Bottle with bottom half cut off. H. Gas carbon. L. Layer of paraffin poured in on the cork.

acid added to the water was furnishing part of the gases; but it is found that no matter how long the gases are being discharged, the amount of sulphuric acid remains undiminished.

Probably no more careful and comprehensive experimentation has ever been undertaken than that for finding the proportion by weight in which oxygen and hydrogen

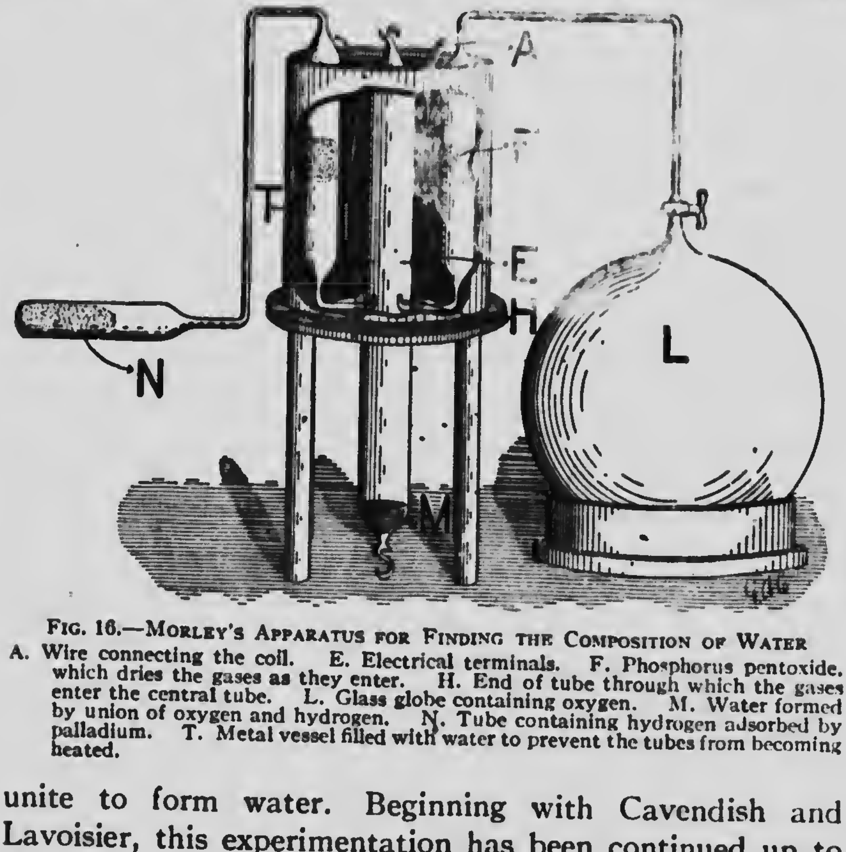

Fig. 16.—Morley's Apparatus for Finding the Composition of Water
A. Wire connecting the coil. E. Electrical terminals. F. Phosphorus pentoxide, which dries the gases as they enter. H. End of tube through which the gases enter the central tube. L. Glass globe containing oxygen. M. Water formed by union of oxygen and hydrogen. N. Tube containing hydrogen adsorbed by palladium. T. Metal vessel filled with water to prevent the tubes from becoming heated.

unite to form water. Beginning with Cavendish and Lavoisier, this experimentation has been continued up to our own time. In 1895 Morley, an American chemist, after five years of arduous work, completed with the apparatus represented in Figure 16, the most accurate set of experiments ever performed.

A glass globe (L) had a known weight of pure, dry oxygen stored in it. The hydrogen was contained in a small glass tube (N) adsorbed in a metal palladium and was driven out by heating the palladium. Both gases were led into the chamber (M) through the tubes (F) (which contained a drying agent to take the last trace of moisture from it). The mixed gases were led in a slow, steady stream, and were continually exploded by the electric spark. In this way large quantities of the gases were exploded, and a considerable quantity of water was formed. The quantity of water was ascertained by weighing the tube (M) before and after the gases were admitted and exploded. The quantities of hydrogen and oxygen were obtained by weighing the tube and globe, respectively, in which they were stored, before and after the experiment. After numerous precautions involving infinite pains and the greatest care and patience, the average of eleven successful experiments was:

Hydrogen used................	3.7198 grams,
Oxygen used...................	29.5335 grams,
Water formed.................	33.2530 grams,

so that 16 grams of oxygen unite with 2.016 grams of hydrogen to form 18.016 grams of water.

Dumas had estimated this ratio with great accuracy fifty years earlier by a quite different method. He undertook the experiment fifty times, but completed it successfully only nineteen times. After spending days in preparing an experiment, he would begin the actual performance very early in the morning, and generally the sun of the succeeding day was far above the horizon before he had completed his observations. This will give the pupil an idea of the kind of work that has been necessary to obtain the quantitative results of chemistry. Figure 17 shows his apparatus set up. He produced hydrogen from a metal and acid, passed it through several U-tubes to absorb the various impurities mixed with the hydrogen, and then passed it over copper oxide heated in a bulb. The water formed was collected in a bulb and a series of U-tubes.

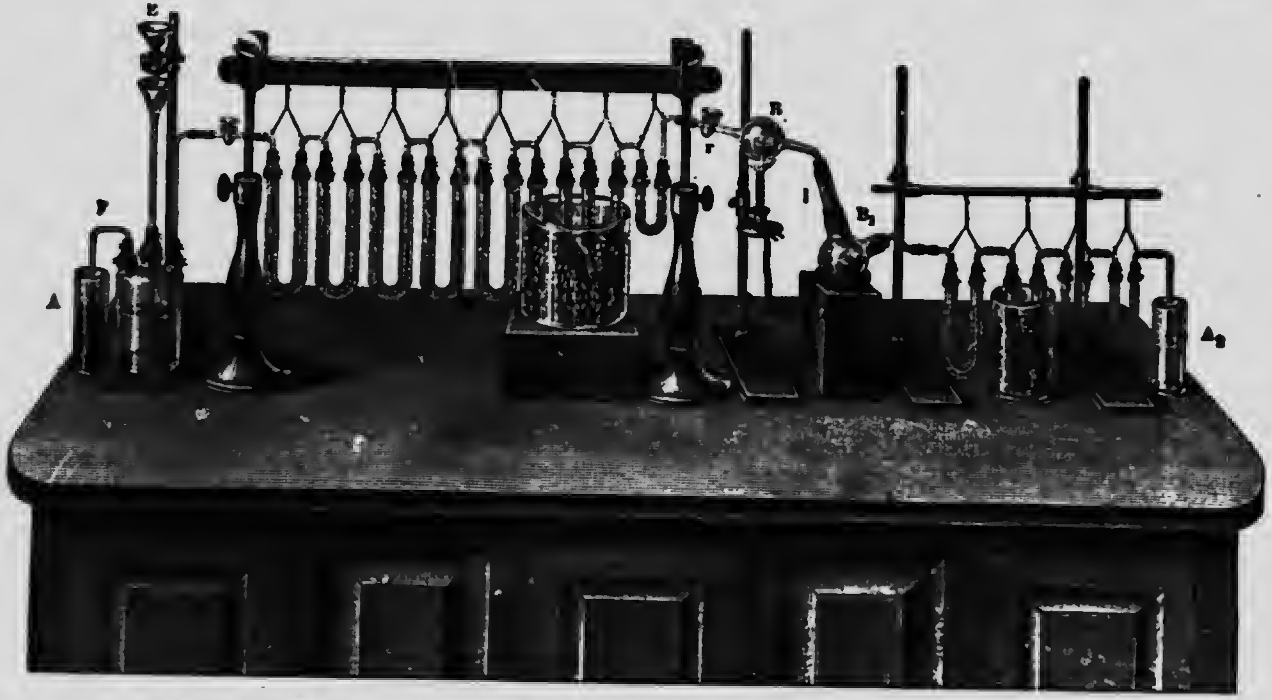

FIG. 17.—FACSIMILE OF APPARATUS USED BY DUMAS FOR FINDING THE COMPOSITION OF WATER

E. Hydrogen generator. The U-tubes contain reagents to absorb the various impurities from the hydrogen; the last two large ones contain phosphorus pentoxide, and are immersed in a freezing-mixture to absorb moisture. The small U-tube just to the right of the freezing-mixture also contains phosphorus pentoxide. It is weighed before and after the experiment to be certain that the gas is perfectly dry. B. Bulb containing copper oxide. This is weighed before and after the experiment. B_1. Bulb in which the water formed is collected. To the right of this bulb are U-tubes containing reagents to absorb the last trace of moisture. This bulb and these tubes are weighed before and after the experiment. A_2. A vessel containing sulphuric acid, through which the unused hydrogen bubbles.

HYDROGEN

"Thus water, independently of oxygen, which is one of its constituents, and which is common to it along with many other substances, contains another constituent which is peculiar to it, which is its constituent radicle and to which we find ourselves compelled to give a name. None has appeared to us more suitable than hydrogen, that is to say "generative principle of water", from *hudor*, water, and *gen* to generate. We shall call hydrogen gas the combination of this principle with heat, and the word hydrogen alone will express the base of this same gas, the radicle of water." —*Antoine Laurent Lavoisier, 1789*

44. History.—As early as the sixteenth century, it was recognized that when acids were poured on metals a gas was produced, but this gas was not distinguished from air. Cavendish was the first to study seriously the properties of the gas. He recognized that it burned in air and called it "inflammable air". Lavoisier after performing the experiment described in Section 41, called it hydrogen, in order to indicate its relation to water. His words in naming it are reproduced in the quotation above.

45. Occurrence.—Not much free hydrogen is present in nature. Small amounts issue from volcanoes. Some is formed in the process of the decay of organic bodies; hence small quantities are found in the atmosphere. Combined with other elements to form compounds, it forms an important constituent of water and of all plants and animals. If free hydrogen is rare on the earth, it is present abundantly in the atmosphere of the sun. Great solar prominences projecting hundreds of thousands of miles and large enough to envelop a hundred earths are permeated with the incandescent vapour of this element.

46. Preparation.—We have already described one important method of preparation, namely, by the action of metals on water (Sec. 41). Sodium, potassium, and calcium act on water at ordinary temperatures; magnesium, iron, zinc, and aluminium only at a high temperature; while copper, mercury, silver, and gold will not decompose it at any temperature.

Hydrogen is usually prepared in the laboratory by the action of either hydrochloric or sulphuric acid on magnesium, iron, or zinc.

Figure 18 shows a good form of apparatus for preparing hydrogen by this method. Granulated zinc is slid gently down the flask, and dilute sulphuric acid is added through the thistle-tube. The thistle-tube is useful, not only for adding acid to the zinc from time to time as it is required, but also as a safety-valve, if the exit for the gas becomes blocked in any way. Its use in this respect can be readily demonstrated by pinching the rubber delivery tube. Immediately the accumulation of gas in the flask increases the pressure and forces the liquid up the thistle-tube, where it finally overflows. Pupils should always remember that the ascent of liquid in the thistle-tube indicates an impediment to the free passage of gas through the delivery tube. If the hydrogen does not come off freely, the addition of a little blue vitriol solution will accelerate the action. The copper of the vitriol is deposited on the zinc, and thus the action is assisted. The hydrogen is usually collected by the displacement of water. But

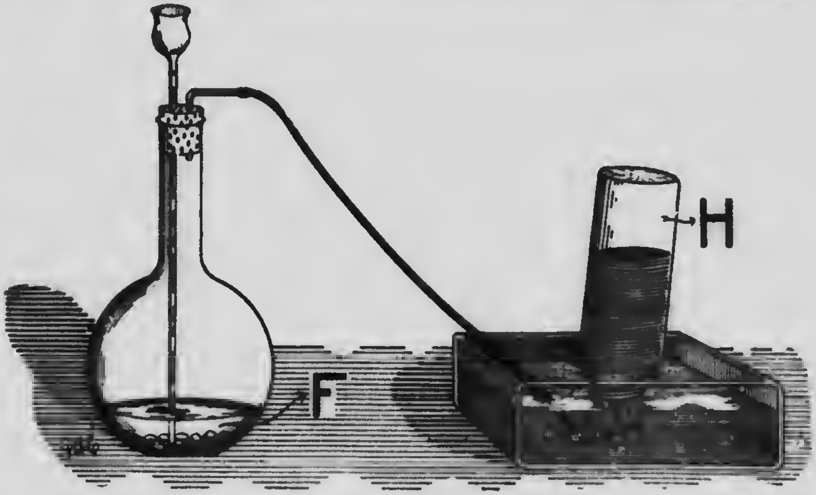

FIG. 18.—PREPARATION OF HYDROGEN
F. Flask containing zinc and sulphuric acid. H. Bottle in which hydrogen is collected.

it may be collected in an inverted gas bottle by the displacement of air, the delivery tube extending to the bottom of the bottle. Many dark particles remain floating in the liquid after the zinc has been all dissolved. These are insoluble impurities in the zinc and would be absent if the pure metal were used.

After these impurities have been filtered out, if the liquid in the flask is evaporated slowly, beautiful clear crystals of a salt called *zinc sulphate* remain behind. The zinc has liberated the hydrogen from the acid and has taken its place. The new substance, with zinc substituted for hydrogen in the acid, is the zinc sulphate. We may indicate the reaction in this form:

Sulphuric acid+zinc→zinc sulphate+hydrogen.

47. Physical properties.—Hydrogen is a colourless gas without taste or smell. It is the lightest of all gases. It is as much lighter than air as water is lighter than mercury. 1 gram occupies 11.12 litres, or one litre weighs .09 grams, the volume in both cases being measured at 0°C. and 760 mm. pressure. With one exception it was the very last gas to be liquefied. In 1898 Sir James Dewar, after surmounting immense difficulties, succeeded in collecting 200 c.c. of liquid hydrogen in the course of five minutes. Faraday, Dumas, and many other chemists had prophesied that if it was ever liquefied or solidified, it would prove to be metallic in appearance. In this they were quite mistaken, as Dewar's vessel of hydrogen was as clear and colourless as water. The solid hydrogen, which was later produced, was also quite colourless. As hydrogen gas is the lightest gas, so liquid hydrogen is the lightest liquid. Water is fourteen times as heavy as liquid hydrogen, so that a piece of cork would sink in it as readily as a stone in a vessel of water.

48. Chemical properties.—The most striking chemical property of hydrogen is its inflammability. When a burning splint is brought to the mouth of a bottle of this gas, the latter burns with a pale blue flame. If the splint is thrust up into the bottle, the flame on the splint is at once extinguished, showing that hydrogen will not support the combustion of wood. When the splint is withdrawn, it is rekindled by the hydrogen burning at the mouth of the bottle. The burning of hydrogen can be well demonstrated by placing a glass tube, drawn to a fine jet, on the end of the delivery tube of the hydrogen generator illustrated in Figure 19. When lit, this hydrogen burns with a pale flame that soon assumes a yellow colour due to the glass. If the gas burns at the end of a gas tip, the flame is almost colourless. When by the displacement of air hydrogen is collected in a dry bottle and ignited, a mist is deposited on the inside of the bottle. This would lead one to think that perhaps water is a product of combustion. The amount of the deposit formed by this method is too small to test, but a much larger quantity can be obtained by the apparatus illustrated in Figure 20. An ordinary hydrogen generator has connected with its delivery tube a U-tube containing calcium chloride, which dries the gas. The hydrogen is lit at the end of a jet, and the flame plays against the surface of a glass retort kept cool by having cold water in it. The liquid is condensed on this cold surface and falls in drops into the vessel beneath. In half an hour a sufficient quantity will be produced. If a piece of sodium is placed on the liquid,

FIG. 19.—APPARATUS FOR BURNING HYDROGEN AT END OF A JET

it generates hydrogen and acts in every way as if the liquid were water. A lump of white anhydrous copper sulphate brought in contact with it at once turns blue. Hence the liquid produced is undoubtedly water (Sec. 40). Thus we have proved again that water is composed of hydrogen and oxygen; for we may assume that it is the oxygen of the air with which the hydrogen has united since the nitrogen is quite inactive toward hydrogen in these circumstances.

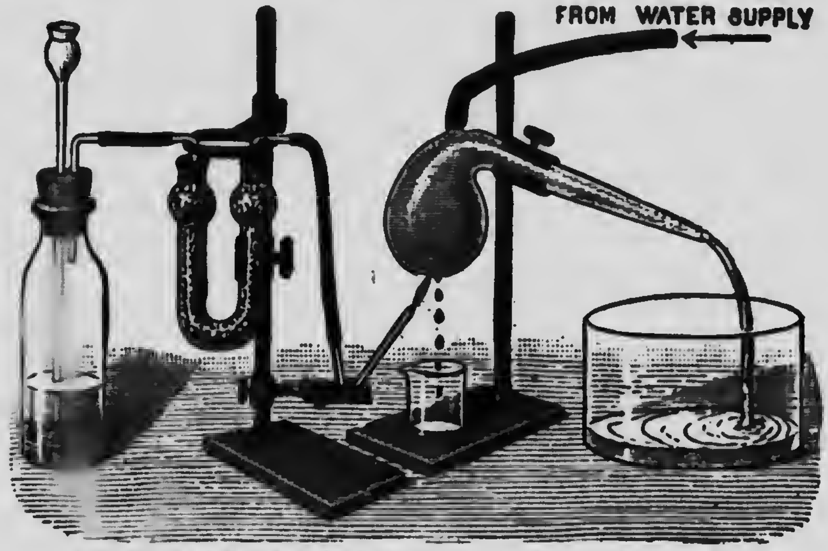

FIG. 20.—APPARATUS FOR SHOWING THAT WHEN HYDROGEN BURNS WATER IS FORMED

The most outstanding chemical property of hydrogen is its ability to unite with oxygen. It will withdraw the oxygen from many compounds which contain the latter. Thus if copper oxide, mercury oxide, iron oxide, or zinc oxide is heated strongly in a crucible, and hydrogen is passed over it, the oxide is rapidly converted into the metal—copper, mercury, iron, or zinc; and the oxygen and hydrogen unite to form water. The apparatus of Figure 21 may be utilized for this purpose. Hydrogen, generated in A, is passed through E, which contains water to wash out impurities, thence through F, which contains calcium chloride to dry it, and finally through H, a combustion tube containing the metallic oxide. The water thus formed is collected in the test-tube (L), which is partially immersed in cold water to assist the condensation of the steam. A substance like hydrogen that extracts oxygen from its compounds is called a *reducer*, and the process is called *reduction*. We shall meet many examples of this process as we proceed.

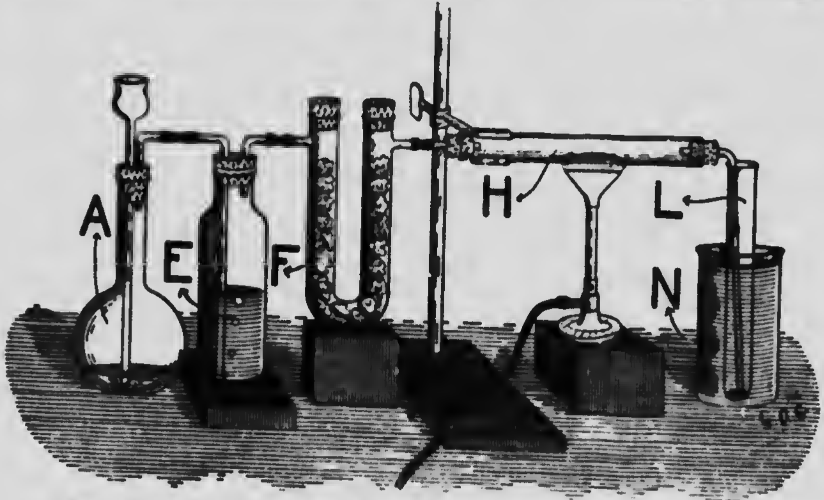

FIG. 21.—APPARATUS TO SHOW THE REDUCING POWER OF HYDROGEN

A. Hydrogen generator. E. Bottle containing water to absorb any soluble impurities in the hydrogen. F. Tube containing calcium chloride to dry the gas. H. Combustion tube containing copper oxide. L. Test-tube to collect the water. N. Beaker containing water to keep the test-tube cool.

If hydrogen and oxygen are mixed and ignited, they combine with a violent explosion. As air contains oxygen, a mixture of it with hydrogen also explodes when ignited, but less violently than when pure oxygen is used. This can be easily demonstrated to a class by placing a few lumps of zinc in a ginger-ale bottle. Then add some dilute acid, and insert a cork, which has an opening stopped by a piece of a clay-pipe stem. If a burning match is held at the opening in the stem, in a short time the gases will ignite and blow the cork out with great violence. It is dangerous to light a jet of the gas connected with a generator, unless it is quite certain that all the air has been driven from all the apparatus. Otherwise the mixed gases will explode, and many have been injured by such accidents. The explosion is due to the sudden expansion of the steam that has been formed by the great heat produced by the union of the oxygen and hydrogen.

49. Commercial importance.—The commercial value of hydrogen is limited. It is used to burn with oxygen in the oxy-hydrogen blow-pipe, which produces a flame of intense heat, but this blow-pipe is now frequently replaced by the electric furnace or the oxy-acetylene flame. Hydrogen is also largely used for the inflating of balloons and airships. England produces the hydrogen which she requires for this purpose by passing steam over red-hot iron; Germany produces hers by decomposing water by electricity; and France, by acting on calcium hydride with water. Hydrogen is often condensed in metal cylinders and is on the market in Canada as a commercial commodity.

50. Test.—Hydrogen can generally be distinguished from other colourless gases by its great lightness, its explosiveness when mixed with air, and by the fact that water alone is formed on combustion.

QUESTIONS

1. Describe three methods of showing that hydrogen is lighter than air.

2. What objection is there to using hydrogen as an illuminating gas or as a fuel?

3. In what way does a mixture of hydrogen and oxygen differ from water?

4. Name several substances that contain hydrogen, and suggest a method of obtaining hydrogen from them.

5. A safe method of lighting a jet of hydrogen is to place a test-tube over it, until the tube is full of the gas. Then bring the test-tube, mouth down, to a flame, and finally ignite the jet with the burning gas at the open end of the test-tube. Explain why this is safe, while putting a burning match directly to the jet is dangerous.

6. Four bottles contain respectively oxygen, nitrogen, hydrogen, and air. Describe how you can tell most readily which is in each bottle.

7. Describe three ways of obtaining hydrogen from water.

8. If sulphuric acid contains 2.04 per cent. of hydrogen, how many grams of acid are necessary to produce 85 litres of hydrogen at 0°C. and 760 mm. pressure? How many litres of hydrogen can be prepared from 750 grams of sulphuric acid?

9. How many litres of hydrogen at 0°C. and 760 mm. pressure can be obtained from 230 grams of water. (Look up in Section 43 the composition of water.)

10. A room 10m.×10m.×7m. contains hydrogen at 0°C. and 760 mm. pressure. What does the hydrogen weigh?

11. A balloon has a capacity of 351,150 cubic feet. What weight of hydrogen is required to fill it at 0°C. and 760 mm. pressure? (1 cubic metre = 35.32 cubic feet.)

12. 5.13 g. of iron filings are placed in a combustion tube, and a current of steam is passed over the filings after they have been heated red-hot. The filings afterwards weigh 5.84 g. What weight and what volume of hydrogen measured at 0°C. and 760 mm. are liberated? (See Section 43.)

13. Dumas in his experiment referred to in this chapter (Sec. 43), found that 840.161 g. of oxygen gave 945.439 g. of water. Find the percentage composition of water.

14. In the experiment of Dumas the following data were obtained:

Weight of copper oxide before heating,	8.12 g.
Weight of copper oxide after heating,	6.92 g.
Weight of calcium chloride and tube before experiment,	49.52 g.
Weight of calcium chloride and tube afterwards.	50.87 g.

From these data calculate the percentage composition of water.

15. 50 c.c. of oxygen and 150 c.c. of hydrogen are passed up into a eudiometer tube and exploded. What volume of gas is left, and how would you prove that it is hydrogen? (See Section 43.)

16. 100 c.c. of hydrogen are passed up into a eudiometer containing 100 c.c. of air, and the mixture is exploded. 137 c.c. of gas is left. From these data calculate the percentage composition of air by volume. (Find the total shrinkage in volume. What part of it was oxygen? What part hydrogen? How much hydrogen remained unused? Of what is the remainder of the 137 c.c. composed?)

17. How would you make sure that a certain colourless liquid substance is water?

18. Why does not pure water occur on the earth's surface?

CHAPTER V

THE GAS LAWS

51. Introduction.—A solid or a liquid is quite readily weighed, but the weighing of a gas presents many difficulties. Yet we frequently require to measure the weight of a gas, and this is generally obtained by measuring its volume, and from this calculating its weight. But the volume changes with temperature. Everybody knows that if gas is heated it expands, and if it is cooled it contracts. Moreover, pressure is a very important factor. For instance, while the air in a bicycle tire exerts great pressure, the pressure would be greatly reduced if the same quantity of air were contained in a vessel of much larger volume. Hence, in order that the volume of a gas may give any indication of the quantity, the exact temperature and pressure at which it was measured must be indicated. As the volume of a gas changes in a regular manner with the changes in temperature and pressure, it is essential that the laws of these changes should be known. But before stating these laws, it will be necessary to explain some terms.

Pressure is measured usually in terms of the height of a column of mercury. When we say the pressure of a gas is 76 centimetres, we mean that if the gas were in a cylinder which has a frictionless piston fitted into it, a column of mercury 76 centimetres high would have to be placed on the top of the piston exactly to prevent the pressure of the gas from pushing up the piston. The atmosphere at the level of the ocean exerts a pressure of about 76

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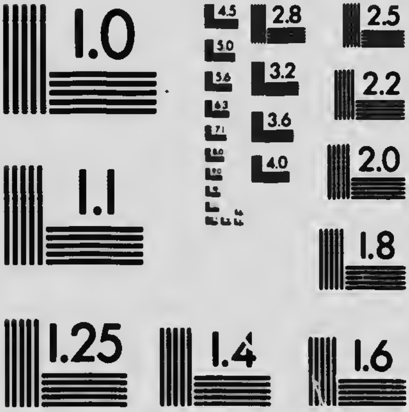

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centimetres, and this is frequently called *normal pressure* or *the pressure of an atmosphere.* Very great pressures, such as those of compressed gases contained in iron cylinders, are measured in atmospheres. Thus a pressure of 200 atmospheres means a pressure 200 times as great as the normal pressure of the atmosphere, and is equivalent to the weight of a column of mercury 76 cm. × 200 or 15200 cm. high.

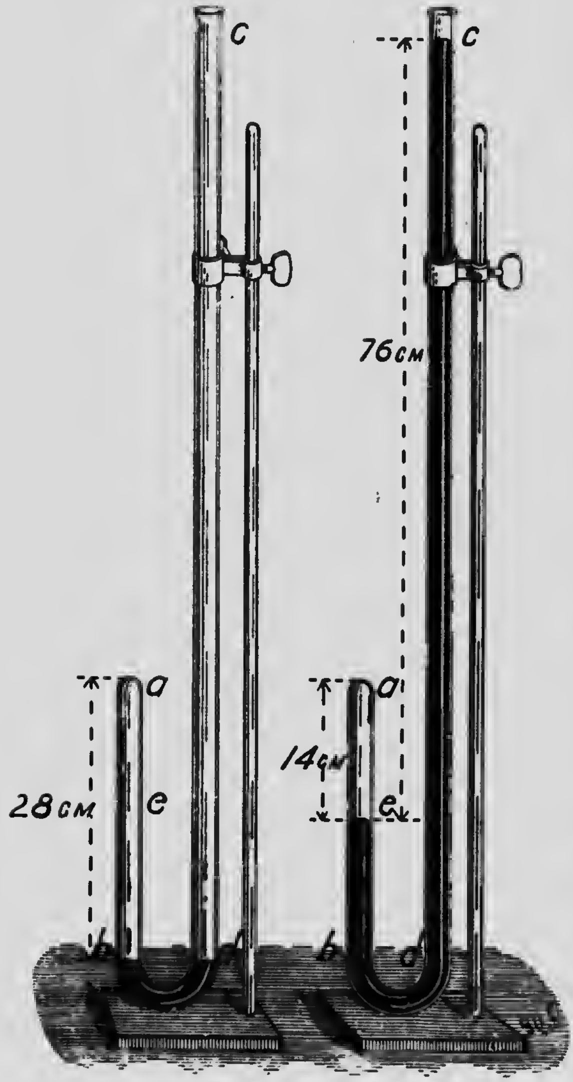


FIG. 22.—TUBE FOR PROVING BOYLE'S LAW

The *normal temperature* selected arbitrarily is 0° centigrade, and normal temperature and pressure will be indicated in this book by the abbreviation N.T.P.

52. Boyle's Law.—About two hundred and fifty years ago, the Honourable Robert Boyle, among the many interesting experiments which he performed, investigated the relation of the pressure and the volume of air in a tube like the one represented in Figure 22. This tube had the short arm sealed at (a) and the long arm open. Mercury was poured in, until it just filled the bend, shutting in the air between (a) and (b) in the short arm. Boyle then measured the length of the air column (a b). Now the downward pressure of the inclosed air on the mercury must just equal the downward pressure of the outside air on the mercury through the long arm, which is 76 cm. Mercury was then poured into the long arm, until the inclosed air occupied only one half of the space it filled previously. When the length of the column of mercury from the level of (e) to the top was measured, it was found to Boyle's delight to be 76 cm., indicating that the pressure was doubled. In Boyle's own quaint words: "Here the same air being brought to a degree of density about twice as great as that it had before, obtains a spring (pressure) twice as strong as formerly". If, again, the pressure is made three times as great, the volume contracts to one third of what it was formerly. From these experiments is deduced the conclusion, appropriately known as *Boyle's Law*, that *the volume of a given quantity of gas varies inversely as the pressure it exerts, the temperature remaining the same.* Suppose a cylinder (Fig. 23) containing some gas is fitted with a

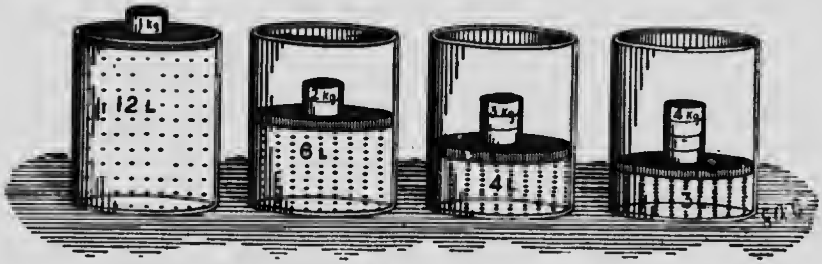


FIG. 23.—RELATIONSHIP OF VOLUME TO PRESSURE IN GASES
(Air pressure neglected)

piston sliding in it without friction, and that when the piston is weighted to 1 kg. the gas occupies 12 litres. Then, if it is weighted to 2 kg., the gas contracts to 6 litres. With 3 kg. pressure the gas contracts to 4 litres, and with 4 kg. pressure it shrinks to 3 litres.

53. Charles's Law.——

> "The results of several experiments made upon hydrogenous, oxygenous, carbonic acid gas, and nitrous gas, which were all the kinds I tried, agreed with those of common air. . . . Upon the whole, therefore, I see no sufficient reason why we may not conclude that all elastic fluids (gases) under the same pressure expand equally by heat." —*John Dalton, 1801*

A piece of thermometer tubing about forty centimetres long is sealed at one end. While the tube is immersed in melting ice, a little column of mercury about two millimetres long is pushed into it by means of a thin iron wire, so as to inclose a column of air in the tube exactly 273 millimetres long. If the tube is heated from 0°C. to 10°C., the air column becomes 283 millimetres long; if the temperature is raised to 100°C., the air column becomes 373 millimetres long. Thus the volume increases 1 millimetre in length, or $\frac{1}{273}$ of its volume at 0°C., for every degree its temperature is raised. If the temperature of the air column is lowered from 0°C. to –1°C., its length shrinks to 272 millimetres; if lowered to –10°C., it becomes 263 millimetres long. Thus each millimetre on the tube represents 1 centigrade degree, and if graduations of the same length be made to the bottom of the tube, the one at the bottom will register –273°C. Every other gas, if placed in the tube, would act in the same manner, and so we can say that equal volumes of all gases under the same pressure expand equally for the same increase of temperature.

No fewer than three scientists share the honour of discovering this law. Charles of Paris discovered in 1787 the relation between the volume and temperature of a single gas, but never published his results. In 1801, Dalton discovered that different gases expand at the same rate for the same change of temperature, and published his results in the words quoted at the head of this section. The next year Gay-Lussac discovered independently the same facts as Dalton. As each of the two last named men already has the honour of having a law named after him, this law is usually called after its first discoverer, *Charles's Law.* In obeying this law, gases are quite different from solids and liquids, for different solids and liquids expand at quite different rates. Aluminium expands more than twenty times as much as platinum for the same change of temperature, while alcohol expands more rapidly than either petroleum or water.

Two kinds of thermometer scales are used in reckoning temperatures in science, the absolute and the centigrade, with the latter of which it is assumed the pupils are familiar. The tube described on page 72 would be suitable for an absolute thermometer, and the zero would be the bottom of the tube. Every millimetre would represent a degree, so that 273° would be the melting-point of ice, and 373° would represent the boiling-point of water. There are thus 100 absolute degrees between these two fixed points; and, as there are 100 centigrade degrees between the same two points, degrees on the two thermometers are equal, a degree in each case being represented by one millimetre on the above tube. Figure 24 shows the tube with absolute degrees marked on one side and centigrade degrees on the other, and it shows clearly that to convert an absolute temperature to a centigrade temperature, 273 must be added to it, and to convert a centigrade

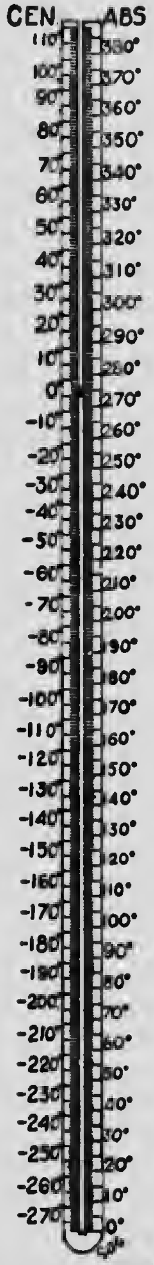


FIG. 24.—A THERMOMETER MARKED IN ABSOLUTE AND CENT. DEGREES

temperature to an absolute; 273 must be subtracted. We have also seen from the expansion of the air in the tube just described that the following relation holds:

The gas occupies 100 mm. in the tube, when the absolute temperature is 100°.

The gas occupies 120 mm. in the tube, when the absolute temperature is 120°.

The gas occupies 200 mm. in the tube, when the absolute temperature is 200°.

The gas occupies 273 mm. in the tube, when the absolute temperature is 273°.

The gas occupies 373 mm. in the tube, when the absolute temperature is 373°.

From the foregoing data we conclude that *the volume of a gas varies directly as the absolute temperature, the pressure remaining constant.* The pupil must not, however, infer from the foregoing that the number representing the volume is always the same as the number representing the absolute temperature, for such an inference is, evidently, quite wrong. This peculiar relation is the result of having purposely made the air column in the tube 273 millimetres long at 0°C. If the air column had been made one half, or one third, or one fifth this length, the lengths at 100°, 120°, 200°, 273°, 373° absolute temperature, would have been respectively one half, one third, one fifth of the lengths given above; yet they would in each case be proportional to the absolute temperature.

54. Solution of problems involving Boyle's and Charles's Laws.—If the volume of a certain sample of gas is measured on two successive days, it will probably be found that the temperature and the pressure have changed, and hence that the volume also has changed. Consequently, if we wish to compare the volumes of two quantities of a gas, it is necessary to find the volume that each would occupy at a given temperature and pressure. Such a problem has frequently to be solved in chemical work.

Example 1. If 300 litres of air are measured at 25°C. and 780 mm. pressure, what volume would the air occupy at 0°C. and 760 mm. pressure?

$$25°\text{C.} = 25° + 273° = 298°\text{A.}$$
$$0°\text{C.} = 0° + 273° = 273°\text{A.}$$

	Temperature	Pressure	Volume
First case.......	298°A.	780 mm.	300 litres
Second case.....	273°A.	760 mm.	x litres

As the temperature is *lowered* from 298°A. to 273°A., the volume will *decrease* in the same proportion; therefore the volume at 273°A. is 300 litres$\times\frac{273}{298}$=274.83 litres. As the pressure is *lowered* from 780 mm. to 760 mm., the volume is *increased* in the same proportion; therefore the volume at 760 mm. pressure is 274.83 litres$\times\frac{780}{760}$=282.06 litres. The pupil must learn, after arranging the data as above, to write the solution as follows:

$$300 \text{ litres} \times \frac{273}{298} \times \frac{780}{760} = 282.06 \text{ litres.}$$

The above solution is applicable to all such questions, and the steps should be taken always in the following order:

(1) Reduce all temperatures to absolute degrees.

(2) Place the data in the foregoing order, having the volumes last, and putting x for the unknown quantity.

(3) Put down the first volume, and multiply it by the two fractions that change it for changes in temperature and pressure, and equate this with the second volume.

(4) Solve for x.

Example 2. If 300 litres of gas measured at 35°C. and 800 mm. pressure have the pressure increased to 1100 mm., to what temperature must the gas be raised, in order that it will still occupy the same volume?

(1) $35°\text{C.} = 35° + 273° = 308°\text{A.}$

(2)

	Temperature	Pressure	Volume
First............	308°A.	800 mm.	300 litres
Second..........	x °A.	1100 mm.	300 litres

(3) $300 \text{ litres} \times \frac{x}{308} \times \frac{800}{1100} = 300 \text{ litres.}$

(4) $x = \frac{300}{300} \times \frac{1100}{800} \times \frac{308}{1} = 423.5°\text{A. or } 423.5° - 273° =$ 150.5°C.

Example 3. Calculate the weight of 1000 litres of oxygen, measured at 25°C. and 740 mm. pressure, when 1 litre at N.T.P. weighs 1.43 grams.

	Temperature	Pressure	Volume
First.........	298°A.	740 mm.	1000
Second.......	273°A.	760 mm.	x

1000 litres at 25°C. and 740 mm. would become 1000 litres $\times\frac{273}{298}\times\frac{740}{760}$ at N.T.P.

1 litre at N.T.P. weighs......................1.43 g.

$1000\times\frac{273}{298}\times\frac{740}{760}$ " " " " $1.43\text{ g.}\times1000\times\frac{273}{298}\times\frac{740}{760}$

$= 1275.6\text{ g.}$

55. The kinetic theory of gases.—This like behaviour of all gases under changes of temperature and pressure is most remarkable, and because they have these and other properties in common, they are assumed to have something common in their construction. The theory brought forward to explain this common behaviour of all gases is called the *kinetic theory of gases.* It supposes all gases to be composed of very small particles called *molecules.* These molecules are all exactly alike in size and weight for the same substance, but are different in different substances. In gases the molecules are separated by spaces much greater than the size of the molecules, and the molecules are not at rest in these spaces, but are moving rapidly in straight lines. When one strikes another, it is reflected along another straight line. The hotter the gas, the more rapidly these molecules move. The pressure of a gas on the walls of its container is due to the continuous bombardment of the walls by the molecules, and the greater the number of molecules bombarding a given area and the more swiftly they are moving, the greater the pressure. If a gas is compressed, the molecules are brought closer together, and hence more of them strike a square centimetre of wall in a given time, and the pressure is therefore increased. If the gas is heated in a closed vessel, the velocity of the molecules increases, and hence they strike the wall harder blows, and the pressure is increased. If the top of a vessel is left open, the gas will escape and diffuse into the air, as the molecules are always moving. To explain further this like conduct of different gases under changes of temperature or pressure *Avogadro* enunciated his notable hypothesis that *equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules.* Hence the structure of the different gases is very much alike, as the molecules are equally far apart no matter what the gas may be.

QUESTIONS

1. If 38 litres of a gas are measured at 60°C. and 555 mm. pressure, find the volume of the gas at N.T.P.

2. If 200 litres of air are measured at 20°C. and 879 mm. pressure, find the volume of the air at 45°C. and 800 mm.pressure.

3. If 600 litres of air at atmospheric pressure are compressed into a cylinder, and the pressure is then found to be 20 atmospheres, what is the volume of the cylinder, if the temperature of the air remains constant?

4. A fire balloon contains 1000 litres of air at 114°C. How much lighter is this than 1000 litres of air at 0°C.? (Sec. 24)

5. A flask of 441 c.c. capacity is surrounded by water and heated up to 80°C. A cork is then inserted into the mouth of the flask, which is immersed in a mixture of ice and water with the mouth down. If the cork is then withdrawn, 100 c.c. of water enter the bottle. Show that the volume of the gas has varied as its absolute temperature.

6. Calculate the weight of hydrogen in a vessel of 10 litres capacity filled at 756 mm. pressure and a temperature of 18°C. (Sec. 47)

7. Find the capacity in cubic inches of a steel cylinder which contains under a pressure of 1,800 pounds per square inch enough oxygen to fill 20 cubic feet under a pressure of 15 pounds per square inch. (Assume Boyle's Law to hold at high pressures.)

8. How many pounds pressure would be required to force 40 cubic feet of coal-gas at 15 pounds pressure into ½ cubic foot?

9. A 500 c.c. and a 1000 c.c. flask are connected by a stop-cock. The large flask is exhausted by the air-pump; the small flask is filled

with air at 750 mm. pressure. Find what the pressure in the flasks will be after the stop-cock is opened.

10. A graduated tube, filled with mercury and inverted in mercury in a trough, has hydrogen passed into it until the volume of gas reads 30 c.c. The mercury in the tube stands 15 cm. higher than the mercury in the trough; the barometer stands at 755 mm. What is the pressure of the hydrogen? What volume will it occupy, if the tube is lowered until the mercury is at the same level inside and outside the tube?

11. Some oxygen is collected in a cylinder over water. There are 200 c.c. of gas in the cylinder, and the water in the cylinder stands 50 cm. higher than the water outside. What volume of oxygen would there be in the cylinder when the water level was the same inside and outside? The water barometer stands at 1000 cm.

CHAPTER VI

SOLUTIONS

56. Solution of a solid in a liquid.—If a small lump of pure sugar is placed in a glass of pure water, everyone has observed that the lump gradually becomes smaller and finally disappears entirely. There is no change in the appearance of the liquid, and yet, if tasted at the top of the glass, it is found to be slightly sweet. This sweetness increases in proportion as the sample is taken from nearer the bottom, indicating that there is more of the sugar in the water close to where the lump rested. However, if the glass is left perfectly still, in time the water will be found to be equally sweet throughout, indicating that the sugar has diffused equally into all parts of the water. The mixture is called a *solution;* the water in which the sugar dissolves is called the *solvent;* and the sugar is called the *solute* or dissolved substance. If the glass containing the solution is held up between the eye and the light, it will be observed that the solution is perfectly transparent and shows no signs of cloudiness, and even if a drop of it is examined under the most powerful microscope, no particles of sugar can be detected. Hence one characteristic of a solution is that it is always *homogeneous.*

The rate of solution naturally depends on the area of contact between the solvent and the solute, for it is only across a surface of contact that the solute can pass into the solvent. If two lumps of sugar are taken, and one is pulverized to a fine powder, the surface of the sugar in that lump has been increased many times. If the powder and the lump are then dropped into separate vessels of water, the powder will dissolve much more rapidly than the lump. Agitation increases the rate of dissolving, as it is constantly bringing new parts of the solvent into contact with the solute. Moreover, if the materials are heated the rate of solution will be increased.

57. Saturated, unsaturated, and supersaturated solutions.—If a little sugar is poured into a test-tube of water, the sugar will disappear rapidly on being shaken, and a solution is formed. If a little more sugar is added, it also disappears on being shaken, but more slowly. If the process is repeated, a stage will soon be reached at which the solution ceases to dissolve the sugar. No matter how long the solution henceforth continues to be shaken, some sugar will remain undissolved at the bottom. Such a solution as this is called a *saturated solution.* The solutions with lesser amounts of sugar dissolved are called *unsaturated solutions.* If to equal quantities of water gradually increasing quantities of sugar are added, a set of an indefinite number of solutions will be obtained, the first being almost pure water and the last being saturated.

If a saturated solution of sugar, with some undissolved solute in the bottom, is heated to a higher temperature, the solution will continue to dissolve more of the solid, until finally it again becomes saturated. Thus the strength of a saturated solution may increase with a rise in temperature. Some substances decrease in solubility with rise in temperature; for instance, if a cold saturated solution of lime is heated, it becomes cloudy, because some of the lime is then deposited out of solution.

Any solution that contains a large proportion of the solute is said to be *concentrated*, while one that contains a small proportion of the solute is said to be *dilute*. These terms, however, are only relative and have no clearly defined meaning.

If a hot, concentrated solution of a substance, whose solubility decreases with a fall in temperature, is cooled slowly without being in contact with the solid solute, it does not follow that the solid will begin to crystallize when the solution becomes saturated. In fact, as a rule it is necessary to cool the solution considerably below this point before crystallization begins. This cooled solution is said to be *supersaturated*. It is stronger, or contains more solute, than the saturated solution. If, however, a particle of the solute, even the minutest grain, is dropped into the supersaturated solution, crystallization always begins at once and continues until the solution is so depleted of the solute that it becomes saturated. This phenomenon can be easily demonstrated as follows. Take half a test-tube of sodium thiosulphate—a salt much used in photography—and add two or three cubic centimetres of water. Then heat it until all the salt is dissolved, and plug the mouth with cotton-wool so as to prevent the entrance of any solid particles. The solution remains clear as long as it is not disturbed, even when it becomes quite cold; yet much more of the salt has been dissolved in the water than would saturate it at that temperature. If the plug is then removed, and the smallest crystal of the salt is added, this crystal, as it sinks through the solution, grows in size, until enough of the salt has been deposited to leave the liquid a saturated solution. Many other salts form supersaturated solutions, when their hot, concentrated solutions are cooled under proper conditions. The only certain way to know whether a clear solution is unsaturated, saturated, or supersaturated, is to drop a crystal of the solute into it. If the crystal decreases in weight, the solution is unsaturated; if the crystal increases in weight, it is supersaturated; and if the crystal remains the same weight, it is saturated.

The *solubility* of a substance is always measured by the amount of solute that is contained in the saturated solution. There is a great difference in the solubility of different substances, and there are various ways of expressing the strength of a solution. Frequently the strength is expressed by stating how many grams of the solute are dissolved in 100 grams of water. Another method is to express it as a certain per cent. A ten per cent. solution is one in which 10 grams of the solute are dissolved in 100 grams of the solution.

58. Solubility curve.—To find the solubility of any salt in water, it is only necessary to be certain that you have a saturated solution of the substance. This is ascertained by shaking excess of the solute with water for a long time. When the undissolved solid has settled, a certain amount of the solution is withdrawn by a pipette and placed in a weighed vessel. The vessel and the solution are again weighed. The solution is then evaporated to perfect dryness and again weighed.

Let us take an example. A saturated solution of saltpetre at 20°C. is prepared, and the following data are found:

Weight of evaporating dish .	36.26 grams
Weight of evaporating dish+solution	69.83 grams
Weight of evaporating dish +saltpetre	44.40 grams
Weight of solution is (69.83–36.26)	=33.57 grams
Weight of saltpetre is (44.40–36.26)	= 8.14 grams
Weight of water is (33.57–8.14)	=25.43 grams

25.43 grams of water dissolve........8.14 grams of saltpetre

100 grams of water dissolve.......8.14 grams$\times\frac{100}{25.43}=$32 grams.

In the same manner it can be found that at 0°, 10°, 30°, 40°, and 50°, 100 grams of water dissolve respectively 13, 21, 46, 64, and 86 grams of saltpetre. These results can be best shown graphically. Indeed, many results in science can be studied much better when expressed in this manner; it is, therefore, highly important that the pupil should be familiar with such a mode of expression. Figure 25 is the graphical expression of the solubility of saltpetre, and K N is called the solubility curve. Two lines A B and A C are drawn at right angles. Along A B are marked off ten equal spaces, each of which represents 10 centigrade degrees. Along A C are marked off a number of equal spaces, each representing 10 grams of saltpetre dissolved in 100 grams of water. Each solubility at each temperature is represented by a point between the two lines. To find the point which expresses the solubility at 20°C., we erect at the 20° mark a perpendicular representing a solubility of 32 grams. This point will be Y. In the same way X represents the solubility at 10°C., and K the solubility at 0°C. The solubilities at 30°, 40°, and 50° are also represented. Now, if a line is drawn through all these points, it is the *solubility curve*, and from it we can determine in an instant the solubility at any temperature, or we can determine the temperature at

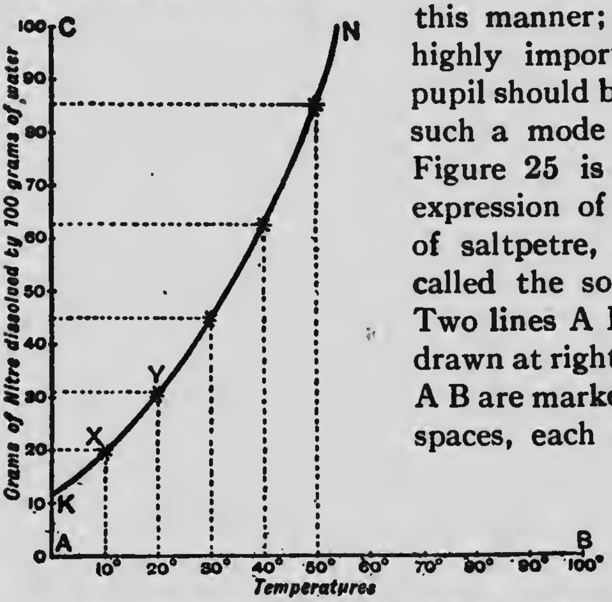


FIG. 25.—GRAPH SHOWING SOLUBILITY CURVE OF SALTPETRE

which any solution becomes saturated. If the paper is ruled off in squares, the points can be determined more

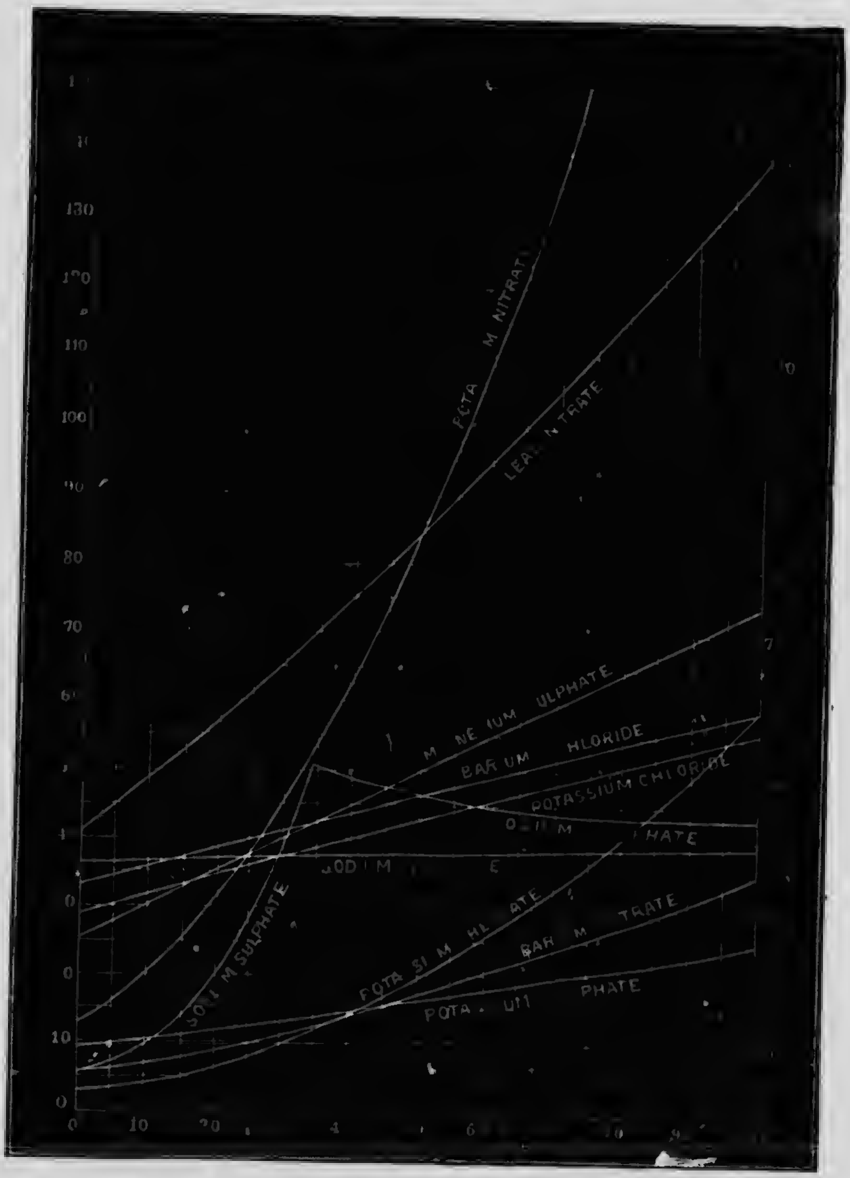


FIG. 26.—SOLUBILITY CURVES OF SOME COMMON SALTS

quickly. Figure 26 shows the solubility curves for a number of salts when dissolved in water.

The term solution, as popularly used, refers to the kinds we have been studying: namely, those produced by a solid and a liquid. In chemistry we extend the meaning to embrace any homogeneous mixture of substances. It will, accordingly, be necessary to study three other classes of solutions: solutions of liquids in gases, solutions of liquids in liquids, and solutions of gases in liquids.

59. Solution of liquids in gases.—When water is in contact with sugar, the latter gradually dissolves in the former. In a similar manner, when air is left in contact with water, the latter gradually dissolves in the former. This we express by saying that the water *evaporates.* Just as there is a limit to the amount of sugar that a given quantity of water will dissolve when the two are in contact, so it is possible to saturate air with water. We then say that the air is saturated or at its dew-point. If the air is cooled below this point, it becomes supersaturated and may fall through many degrees without any water being precipitated; but if the air contains any solid particles, such as dust, the dissolved water will form around these just as the crystal of solute, when dropped into the supersaturated solution, grows in size owing to the deposit of solute on its surface. Fog is more common in smoky cities than in adjoining rural districts, not because the urban air becomes cooled more frequently below its dew-point, but because there are many solid particles in the air (smoke), about which the water in the supersaturated solution can collect, and thus the air is prevented from remaining in a state of supersaturation. In rural districts, where the air is clear, it remains much more frequently in a supersaturated condition.

60. Solutions of liquids in liquids.—If a drop of alcohol is shaken with some water in a test-tube, it dissolves completely. In fact, no matter in what proportion these are mixed, they form one homogeneous mixture. But when ether and water are shaken together, the mixture differs markedly from the former one. If one drop of ether is added to half a test-tubeful of water and the test-tube is thoroughly shaken, the drop dissolves entirely. As more ether is added, the water becomes saturated. Any additional ether, being much lighter than water, floats on the top. Now, if the two layers are separated into two test-tubes, it can be proved that the bottom layer is water with ether dissolved in it, while the top layer is ether with water dissolved in it. Hence we can say, that mutually they are slightly soluble. If benzine and water are treated in the same way as the ether and water, it is found that the liquids also divide into two layers, but that the lower one is pure water and the upper one pure benzine. Thus, pairs of liquids divide themselves into the three classes: (1) Those that are mutually soluble in all proportions, (2) those that are mutually soluble up to a certain limit, after which they separate into layers, and (3) those that are mutually insoluble.

61. Solubility of gases in liquids.—If cold water from the tap is allowed to stand in a warm place, small bubbles of a gas soon appear on the sides and bottom of the vessel containing it. This gas is composed chiefly of oxygen and nitrogen that were dissolved in the water, and the phenomenon indicates that the solubility of a gas in a liquid decreases with a rise of temperature. In this respect the action of a liquid is in most cases different toward gases from what it is toward solids; for the solubilities of the latter, we have seen, usually increase with a rise of temperature. The same phenomenon is observed when a vessel of water is boiled. While the water is still only moderately warm, bubbles are observed to rise from it. These, of course, are composed of oxygen and nitrogen, because bubbles of steam do not begin to form until the temperature has risen to 100° C.

Some gases dissolve much more readily in water than does air. At ordinary temperatures water will dissolve nearly its own volume of carbon dioxide and many times its volume of ammonia. A given volume of a liquid will dissolve the same volume of a gas, no matter what pressure the gas exerts. Hence, if the pressure of a gas is doubled, a cubic centimetre of liquid will dissolve twice as great a weight of it, for the same volume contains twice as great a weight of gas at the higher pressure. The effect of pressure on the solubility of a gas is well shown in such "soft" drinks as soda-water, ginger-ale, etc. These are all composed of ordinary water with carbon dioxide in solution, the gas having been dissolved under a pressure of two or three atmospheres. When they are uncorked, the pressure decreases to that of the atmosphere, and large quantities of carbon dioxide escape.

Other liquids besides water dissolve gases, but different liquids differ greatly in the quantities of gases that they dissolve.

62. The role of dissolved gases in water.—The solution of oxygen and carbon dioxide in water plays a very important role in the life processes of aquatic plants and animals. Without these gases in the water, every stream, lake, or sea would be utterly devoid of plants and animals that respire under water. The animals depend entirely upon the dissolved oxygen for respiration; and the green plants depend on the dissolved carbon dioxide for building up the tissues of which they are largely constructed. The dissolved oxygen plays another important part. Every stream and rivulet is pouring large quantities of plant and animal remains into the larger bodies of water, there to decay. It is the dissolved oxygen that converts these putrid remains into harmless and inoffensive substances, and thus keeps the waters pure.

63. Deliquescence.—When a salt dissolves in water, the boiling-point of the solution is raised, and the stronger the solution the higher the boiling-point. In other words, the tendency to give off water vapour is less in a solution than in pure water. If the solution becomes very concentrated, the tendency of water to evaporate from the solution may become so small that, if there is much water vapour in the air, instead of evaporation taking place water may pass from the air into the solution. This takes place usually with sulphuric acid. If sulphuric acid is left exposed to the air, it will increase in weight, owing to the fact that water passes from the air into the acid. If sulphuric acid is left in contact with a confined quantity of air, it will thus tend to dry the air, and a substance that acts in this way is called a *denydrating* or *drying agent.* Many very soluble solids act in the same manner. If a piece of sodium hydroxide is left exposed to the air, it first appears moist and finally the solid entirely dissolves, leaving an aqueous solution of the salt. The sodium hydroxide, like all other solids, has a thin film of water on its surface, the result of condensation from the air. This water dissolves the hydroxide to make a very concentrated solution, which has so little tendency to give off water vapour that it acts like sulphuric acid, and water passes from the air into it rather than in the opposite direction. Thus water passes into the solution, and more of the hydroxide is dissolved, until finally the whole of the hydroxide is mixed with the absorbed water to form a solution. Zinc chloride, calcium chloride, phosphorus pentoxide and all very soluble salts act in a similar manner and are called *deliquescent substances.* The property is called *deliquescence.*

64. Hydrates.—If blue vitriol is heated in a crucible, it decomposes, giving off water vapour and leaving a white amorphous-looking residue. Many other crystalline substances do the same thing, such as sodium sulphate and magnesium sulphate. Salts of this kind are frequently called *hydrates*, and the water thus driven off is called *water of crystallization*, because the residue is not in the form of crystals, and it was formerly believed that this water was necessary for crystallization. However, many other salts crystallize perfectly without water; .and even some that are usually hydrates can be crystallized without water. It is better to view the hydrate and its anhydrous residue as two substances; and the conversion of one into the other as a chemical change.

If the air is very dry, it is not necessary to heat blue vitriol in order that water should pass from it into the air, leaving the amorphous-looking residue behind. On the other hand, if the anhydrous copper sulphate is left in contact with moist air, the former gradually absorbs water from the air, converting the solid back into blue vitriol. Thus the following two reactions may take place according to the humidity of the air:

(1) blue vitriol → anhydrous copper sulphate + water;
(2) anhydrous copper sulphate + water → blue vitriol.

The chemical action expressed by the first equation is called *hydration;* that by the second, *efflorescence.* Washing-soda in crystals is a hydrate, efflorescing in ordinary air and forming a white powder; but, like many other hydrates that have effloresced, it will again combine with the water of the air if the latter is humid enough. A hydrate that effloresces in one climate may not do so in a more humid climate, but, on the contrary, its anhydrous salt may become a hydrate.

65. Theoretical explanation of solution and its related phenomena. — Chemists generally hold that pure substances are composed of small particles called molecules. In the same pure substance these molecules are all of the same size; and are not in permanent contact, but have spaces among them. They are also not at rest, but in motion. When sugar is placed in water, its molecules move in the spaces among the molecules of the water and gradually diffuse until the mixture is uniform. If we consider the phenomenon more closely, we shall see that the process of solution will come to an end in time. Across the surface of contact between the sugar and the water the molecules of sugar pass into the water. As the molecules of sugar continue to mix with the water across the common surface, not only do sugar molecules pass from the sugar to the water, but some of those already in the water pass back again into the sugar. The more the sugar is dissolved, the more rapid does this latter process become. Finally, a state of equilibrium is reached, when just as many molecules leave the sugar to enter the solution as leave the solution to enter the sugar. The sugar will then no longer decrease in size, and we have a saturated solution.

In the case of deliquescent substances (Sec. 63), the molecular theory also offers a simple explanation. In these, molecules of water are passing from the air into the filmy solution on the substance and from the solution into the air, and if the air is humid, the number passing from it into the solution of the deliquescent substance is greater than the number passing in the opposite direction; so water passes from the air into the solution covering the deliquescent substance. This process continues, until the solution of the deliquescent substance becomes so dilute that there is equilibrium between the number of molecules passing in each direction.

66. Pure substances, solutions, and mechanical mixtures.—We have now studied some properties of solutions; it remains to compare them with pure substances on the one hand and with mechanical mixtures on the other. When two substances are placed in contact to form a mechanical mixture, usually nothing happens; they show no tendency to mix of their own accord, no heat is produced or absorbed, and there is no change of volume. The two components remain separate in little lumps, which usually can be detected with the eye or by means of the miscroscope; if one of the components is a liquid, the mixture is never transparent, but is always turbid. The mechanical mixture is, accordingly, always heterogeneous. When two components that will form a solution are placed in contact, they at once begin to mix of their own accord and continue until the mixture becomes homogeneous, provided there is not too much solute. The mixing, except in the case of gaseous solutions, is accompanied by a change of temperature and by a change in volume, the volume of the solution not being the sum of the volumes of its components.

The components in a mechanical mixture possess the same tendency to react as they did before mixing. If a mixture of sand and water is made, the water has the same tendency to boil and freeze as before: that is, it still boils at 100° C. and freezes at 0° C. It has the same tendency to act on sodium or calcium. When components are mixed to form solutions, their tendency to react is always changed, but frequently not to a marked degree. If water is mixed with salt to form a solution, its boiling-point and freezing-point are both changed. While it appears to react with sodium or potassium as vigorously as before, it would be found, if the intensity of the action were accurately measured, that it had changed, and the same is true of all its reactions. Yet the properties of the solution are so related to those of its components, that the reactions of the solution can usually be predicted from a knowledge of the properties of its components.

Compounds, on the other hand, are markedly different from both solutions and mechanical mixtures. They differ from mechanical mixtures in that when they are formed from, or are decomposed into their constituents the process is always accompanied by changes in heat and volume. They differ from solutions in that solutions may be made up into sets, with gradually varying proportions and with properties steadily varying; while compounds cannot be made in such sets—and in this sense have a fixed composition. Moreover, the properties of compounds are often more markedly different from those of their constituents than are the properties of solutions.

QUESTIONS

1. How can the proportions of a soluble and an insoluble solid in a mixture be determined accurately?

2. If you are given a bottle containing a clear solution of copper sulphate, how can you tell most readily whether it is saturated, unsaturated, or supersaturated?

3. 10 c.c. of a saturated salt solution weigh 11.8 grams. After evaporation 3.04 grams of salt remain. Calculate the solubility of salt at this temperature.

4. (*a*) Draw a solubility curve of Epsom salt from the following data:

Temperature.	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
Solubility....	26.9	31.5	36.2	40.9	45.6	50.3	55	59.6	64.2	68.9	73.8

(*b*) If a saturated solution at 90° C. contains 200 grams of the salt, how much will be deposited when it cools to 15° C.?

5. Explain the use of benzine and gasolene as cleaning agents.

6. Kerosene, turpentine, benzine, gasolene, chloroform, and ether, all dissolve fats readily. Which is the most suitable to use for removing grease spots from clothing? Give reasons.

7. Calculate the percentage of water of crystallization in gypsum from the following data: 7 grams of gypsum lose 1.464 grams when heated strongly.

8. From a study of the solubility curves in Figure 26 answer the following questions:

(*a*) Find the number of grams of potassium chloride that would be contained in 100 grams of water saturated with the salt at 10° C., at 30° C., at 50° C.

(*b*) At what temperature do 100 grams of water dissolve equal quantities of potassium chlorate or potassium chloride? How much of each does the water contain at that temperature? If such solutions of each are cooled to 10° C., how much of each salt will be precipitated?

CHAPTER VII

THE LAWS OF COMBINATION

> "The utility of being acquainted with these important laws is almost too manifest to require mention. Through their aid, and by remembering the equivalents of a few elementary substances, the composition of an extensive range of compound bodies may be calculated with facility."
>
> —*Edward Turner, 1833*

67. Law of multiple proportions.—We have already learned how Dalton established the law of definite proportions (Sec. 35), according to which the percentage composition of a pure substance is absolutely invariable. This general statement was, however, not accepted by all the great chemists of the early years of the nineteenth century. In fact, one of the greatest controversies in the history of chemistry raged over this very law. The two leaders in the strife were both French chemists, Proust, who championed the law, and Berthollet, who held that two pure substances react, not in one definite proportion, but in gradually changing proportions within certain limits. Berthollet was mistaken in his view, and his error was due to not having distinguished carefully between pure substances and mixtures. It was, however, soon recognized that elements do frequently unite in more than a single proportion, and that for each proportion in which they unite, or react, a distinct pure substance is formed. The following is the percentage composition of six sets of pure substances, the members of each set of which are composed of the same two elements, the percentages given having been ascertained by quantitative experiments in the laboratory:

(1) Water: 88.81 oxygen, 11.19 hydrogen
Hydrogen peroxide: 94.12 oxygen, 5.88 hydrogen

(2) Ethane: 80 carbon, 20 hydrogen
Methane: 75 carbon, 25 hydrogen

(3) Ferrous sulphide: 63.64 iron, 36.36 sulphur
Pyrite: 46.67 iron, 53.33 sulphur

(4) Cuprous oxide: 88.83 copper, 11.17 oxygen
Cupric oxide: 79.9 copper, 20.1 oxygen

(5) Tin suboxide: 88.15 tin, 11.85 oxygen
Tin oxide: 78.81 tin, 21.19 oxygen

(6) Sulphur dioxide: 50 sulphur, 50 oxygen
Sulphur trioxide: 40 sulphur, 60 oxygen.

Left in this form, these percentage compositions show no significant relationship; but, if for each pair of substances we calculate how much of the second element is united with a fixed quantity of the first (say 100 grams), we discover a most important law of chemistry. If 88.81 grams of oxygen combine with 11.19 grams of hydrogen, then 100 grams of oxygen combine with 11.19 grams $\times \frac{100}{88.81} = 12.5$ grams of hydrogen. The composition of these substances, when stated in this way, is as shown in the table on the next page.

It will be noticed that in each set the amounts of the second element that unite with 100 grams of the first element bear a simple relation to each other. In the first set the amounts of hydrogen in the two substances are in the proportion of one to two, in the second set two to three. On consulting the last column it will be found that the numbers representing the proportions throughout are never greater than two to three. The amounts of the second element in each set have not exactly the proportions indicated by the simple numbers, but that is due to the fact that the percentage compositions given in the list are experimental results (and hence are only approximate), and not to any real variation from the simple proportion; for, the more carefully analyses are made, the more nearly do the proportions of the second element united with a fixed quantity of the first correspond to simple whole numbers. This great principle was named *Dalton's law of multiple proportions*, having been first formulated by that chemist as a deduction from his atomic theory, which will be discussed later in this book. Subsequent experiments soon proved Dalton's deduction to be true in fact.

Name of substance		Amount of second constituent united with 100 grams of first	Proportions of amounts in third column
Water............	100 g. oxygen	12.5 g. hydrogen	2 : 1
Hydrogen peroxide.	100 g. oxygen	6.25g. hydrogen	
Ethane...........	100 g. carbon	25 g. hydrogen	2 : 3
Methane..........	100 g. carbon	33.3 g. hydrogen	
Ferrous sulphide...	100 g. iron	57.14 g. sulphur	1 : 2
Pyrite............	100 g. iron	114.28 g. sulphur	
Cuprous oxide.....	100 g. copper	12.57 g. oxygen	1 : 2
Cupric oxide.......	100 g. copper	25.15 g. oxygen	
Tin suboxide.......	100 g. tin	13.44 g. oxygen	1 : 2
Tin oxide..........	100 g. tin	26.88 g. oxygen	
Sulphur dioxide....	100 g. sulphur	100 g. oxygen	2 : 3
Sulphur trioxide....	100 g. sulphur	150 g. oxygen	

68. Law of combining weights.——

> "Nevertheless, the foundation of all that has been done in developing the subject of chemical equivalency was laid by him (Richter) in the statement that the proportion between the weights of bases which are neutralized by acids is constant and independent of the nature of the acid."
>
> —*Pattison Muir.*

Even before the two great chemical laws stated in Section 67 were discovered and formulated, Richter, a German chemist referred to in the above quotation, had discovered and stated a still more comprehensive law, though he never recognized its universal application, but considered that it applied only to reactions between acids and bases. This law we shall now present, demonstrating at the same time that it is applicable to all pure substances reacting chemically.

In Section 35 it has already been shown how the percentage composition of a compound substance may be obtained experimentally; the following is the percentage composition of six such substances:

(1) Magnesium oxide		(2) Water		(3) Carbon dioxide	
Magnesium	60.40	Hydrogen	11.19	Carbon	27.27
Oxygen	39.60	Oxygen	88.81	Oxygen	72.73
(4) Mercuric oxide		(5) Sodium oxide		(6) Chlorine monoxide	
Mercury	92.59	Sodium	74.19	Chlorine	81.61
Oxygen	7.41	Oxygen	25.81	Oxygen	18.39

Each of these substances contains oxygen as one of its constituents. Instead, however, of calculating the composition as so many grams of each constituent in one hundred grams of substance, we shall select a fixed weight of oxygen, and calculate the weight of each constituent that unites with this fixed weight.

For a reason that will be evident later, we select 8 grams as our fixed weight of oxygen. Now, as in magnesium oxide 39.6 grams of oxygen combine with 60.4 grams of magnesium, 8 grams of oxygen combine with 60.4 grams $\times\frac{8}{39.6}=12.2$ grams of magnesium. In the same way, we find that 8 grams of oxygen combine with 1 gram of hydrogen, 3 grams of carbon, 100 grams of mercury, 23 grams of sodium, and 35.5 grams of chlorine. These names and figures are arranged below in a circle, with the oxygen at the centre. The weight of each constituent that combines with 8 grams of oxygen is placed in an oblong, and a bond is passed from each to the oxygen oblong to indicate that it combines with oxygen.

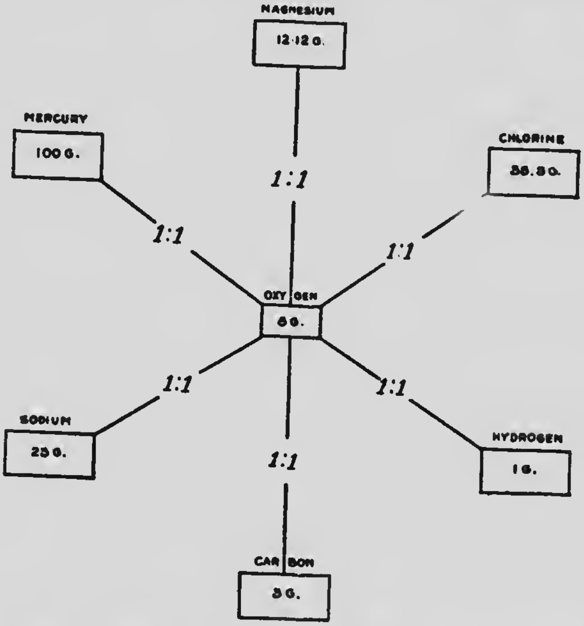


FIG. 27.—DIAGRAM EXPRESSING THE COMBINING RELATIONS OF SEVEN ELEMENTS

If the quantities represented by the numbers in the oblongs are considered the unit quantities, then the elements unite in the proportion of these unit quantities; this is indicated by the ratio 1 : 1, which is placed along the line joining each two elements that were combined in the above compounds.

These six elements which combine with oxygen combine among themselves to form a variety of compounds, and show a remarkable peculiarity in the proportions in which they so combine. The following is the composition of three of these compounds, all of which contain hydrogen as a constituent:

(1) Methane		(2) Hydrogen chloride		(3) Sodium hydride	
Carbon	75	Hydrogen	2.74	Sodium	95.83
Hydrogen	25	Chlorine	97.26	Hydrogen	4.17

Now 1 gram of hydrogen was the quantity we found to combine with 8 grams of oxygen. Let us find with how much carbon, chlorine, and sodium 1 gram of hydrogen is combined in methane, hydrogen chloride, and sodium hydride respectively.

In methane 25 grams of hydrogen are combined with 75 grams of carbon; therefore 1 gram of hydrogen is combined with 3 grams of carbon. In the same way, we find that in the composition of hydrogen chloride and sodium hydride, 1 gram of hydrogen is combined with 35.5 grams of chlorine, and 1 gram of hydrogen with 23 grams of sodium; but 3 grams of carbon, 35.5 grams of chlorine, and 23 grams of sodium are also the amounts of the elements that we found would combine with 8 grams of oxygen; and as chlorine unites with magnesium, with mercury, and with sodium to form magnesium chloride, mercurous chloride, and sodium chloride, the amounts of these elements that unite with 35.5 grams of chlorine are 12.12 grams of magnesium, 100 grams of mercury, and 23 grams of sodium, again the exact quantities that we found combining with 8 grams of oxygen. These new combinations we shall again represent in a circular diagram (Fig. 28).

If we had the seven elements in parcels of the weights indicated in the diagram, then to form a compound of any two of them, it would be necessary only to bring together a parcel of each under such conditions as would result in combination; they would then be in the proper proportions to unite completely, none of either being left over.

From the above facts regarding the compounds of these seven elements, we may state generally that for each element such a weight can be selected that, when these elements take part in a chemical reaction, they will always react in the proportions of these weights.

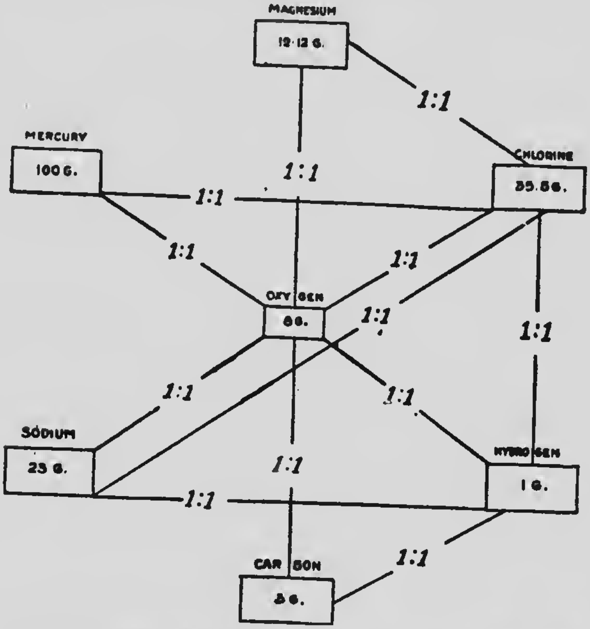


FIG. 28.—DIAGRAM EXPRESSING THE COMBINING RELATIONS OF SEVEN ELEMENTS

But the law is not quite so simple as the above statement would indicate. Besides the mercurous chloride mentioned above, mercury and chlorine unite to form mercuric chloride; but in this case 35.5 grams of chlorine are combined with 200 grams of mercury or 2 parcels. Similarly, 1 parcel of oxygen (8 grams) not only combines with 1 parcel of carbon (3 grams) to form carbon dioxide, but it also combines with 2 parcels (6 grams) to form carbon monoxide. But the numbers of the parcels that react together always form a very simple proportion.

And what is true for these seven elements is true not only for all the elements, but for all pure substances, whether they be elements or compounds. We can thus give the complete statement of the *law of combination* or *of combining weights. For every pure substance such a weight can be selected that, when such substances take part in a reaction, they do so in the proportion of these weights or in simple multiples of these weights.*

Two things should be noticed about the weights selected: (1) The numbers are only relative, their absolute value depending on the initial number—in this case 8 grams of oxygen, for, if 16 grams of oxygen had been selected, the numbers would all have been doubled. (2) Some choice may be exercised in selecting the numbers. We selected 3 grams for carbon, because in carbon dioxide 8 grams of oxygen are combined with 3 grams of carbon; but we might just as well have selected carbon monoxide, in which 8 grams of oxygen are combined with 6 grams of carbon. The combining weight of carbon would then have been 6 grams instead of 3 grams; and in carbon dioxide, in which 3 grams of carbon are combined with 8 grams of oxygen, or 6 grams of carbon with 16 grams of oxygen, 1 combining weight of carbon would have been combined with 2 combining weights of oxygen. The various weights which it is possible to select are called *combining weights* and the particular one which is finally selected is called the *reacting weight.*

If all pure substances used in the chemical laboratories were put up in parcels whose weights were their reacting weights, and if, when any two took part in a reaction, a parcel of each were used, the substances would be present in exactly the correct proportions to react completely, so that none of either would remain unused. Moreover, the weights of the new substances formed would be their reacting weights. If, also, a parcel of zinc were placed in a parcel of sulphuric acid, the two would react completely; no zinc and no acid would remain unused, and just one parcel of hydrogen and one parcel of zinc sulphate would be produced. Of course, it would in some cases be necessary to use two parcels of one with one of the other, or to combine parcels in some other simple ratio.

But from mere investigation of the composition of pure substances, we cannot finally decide which of the possible combining weights is the most suitable to select for each substance. This difficulty proved a stumbling block in the path of the most scholarly chemists during the first half of the nineteenth century, but in 1858 it was finally cleared up by the brilliant young Italian, Cannizzaro, whose method will be presented after we have established Gay-Lussac's law of volumes.

69. Gay-Lussac's law of volumes.—

> "M. Gay-Lussac has shown in an interesting memoir that gases always unite in a very simple proportion by volume, and that when the result of the union is a gas, its volume also is very simply related to those of its components." —*A. Avogadro, 1811*

The following facts have been found by quantitative experiments: 8 g. of oxygen combine with 6 g. of carbon to form 14 g. of carbon monoxide; 1 g. of hydrogen combines with 35.5 g. of chlorine to form 36.5 g. of hydrogen chloride; 1 g. of hydrogen combines with 3 g. of carbon to form 4 g. of methane. Accordingly, as 8 grams and 1 gram are combining weights of oxygen and hydrogen, 14 grams, 36.5 grams, and 4 grams are combining weights of carbon monoxide, hydrogen chloride, and methane.

Let us put in one column the combining weight of each gaseous substance occurring in the foregoing reactions, and, alongside of each, the volume it occupies at N.T.P., as found by experiment:

1	g. of	hydrogen	at N.T.P.	occupies	....11.2	litres
8	g. "	oxygen	"	"	... 5.6	"
35.5	g. "	chlorine	"	"	...11.2	"
14	g. "	carbon monoxide	"	"	...11.2	"
4	g. "	methane	"	"	... 5.6	"
36.5	g. "	hydrogen chloride	"	"	...22.4	"

From the above it is evident that the relation between the volumes of the combining weights of different pure substances is very simple; for the only three volumes occurring are 5.6 litres, 11.2 litres, and 22.4 litres; and 22.4 litres= 5.6 litres x 4; and 11.2 litres=5.6 litres x 2. As these gases, when they react, do so in the proportion of these weights or simple multiples of them, the proportions by volume in which they react must also be very simple. And what is true for these gases is equally true for all gaseous pure substances. Over one hundred years ago Gay-Lussac, having observed the simple proportion existing between the volumes of gases that react, enunciated the law of combination by volume, which is known as *Gay-Lussac's law of volumes*. According to this law, *when gaseous pure substances take part in a reaction, they react in a simple proportion by volume.*

Imagine an experimental laboratory in which only experiments with gases are performed. Containers of only one size will be necessary. All the various gases, both compounds and elements, can be contained in these. When an experiment is performed, it will simply be necessary to take the required number of vessels of each gas, which number will be small in the case of the substances dealt with in elementary chemistry. When the gases are brought together, under suitable conditions, they will react completely, none of either remaining; and, if any gaseous products are formed, the amount will be just sufficient to fill a very simple number, such as one, two, three, or four vessels.

70. Further differences between mixtures and pure substances.—The laws of combining weights and combining volumes supply an additional means of distinguishing solutions and mechanical mixtures on the one hand from compounds on the other; the latter always have their constituents present in the proportion of their combining weights, while the proportions of the components in a mixture may vary greatly and have no relation to their combining weights. For example, an alloy of silver and copper contains 40 per cent. of silver and 60 per cent. of copper, and behaves in some respects like a compound. Let us test whether the elements are present in the proportion of their combining weights, which are 108 grams for silver and 63.6 grams for copper.

Since 60 grams of copper are united with 40 grams of silver, 63.6 grams of copper will unite with 40 grams $\times \frac{63.6}{60} =$ 42.4 grams of silver.

However, 42.4 has no simple relation to 108; it is neither 1/2 nor 1/3, but is about 20/51 of the combining weight of silver. Accordingly, the elements are present neither in the proportion of their combining weights nor in any multiples thereof, and this alloy is not a compound, but a mixture.

QUESTIONS

1. Show that the law of multiple proportions is a particular case of, and deducible from, the law of combining weights.

2. Two oxides of a metal M contain respectively 22.53 per cent. and 30.38 per cent. of oxygen. Show how these two oxides illustrate the law of multiple proportions.

3. An empty porcelain boat weighs 3.428 grams. Some copper filings are placed in it, and then the two weigh 4.278 grams. The boat is heated in a combustion tube through which oxygen is passed, until it ceases to increase in weight. The boat now weighs 4.488 grams. From these data find a combining weight of copper, taking that of oxygen to be 16 grams.

4. If 0.53 grams of magnesium when burned in air produce 0.88 grams of magnesium oxide, calculate a combining weight of magnesium, if that of oxygen is 16 grams.

5. Combining weights of oxygen and nitrogen are 16 grams, and 14.01 grams. The percentage composition of air is nitrogen, 76.995 per cent. and oxygen 23.005 per cent. Are the elements present in air in the proportion of these combining weights or simple multiples of these combining weights? Is air a mixture or a compound? Give reasons for your answer.

6. The combining weight of copper sulphate is 159.6 grams and of water 18 grams. When 1 gram of blue vitriol is heated, 0.64 grams of copper sulphate are left as residue, and 0.36 grams of water are driven off. Is blue vitriol a compound or a mixture? Why?

7. If 1 gram of zinc requires 1.498 grams of sulphuric acid to produce 0.030 grams of hydrogen and 2.468 grams of zinc sulphate, find a combining weight of zinc, of sulphuric acid, and of zinc sulphate, assuming the combining weight of hydrogen to be 1 gram.

CHAPTER VIII

THE SHORTHAND OF CHEMISTRY

71. Molecular or formula weights.—As was done in the preceding chapter, let us place in one column the combining weights of some gaseous pure substances, and alongside of each the volume it occupies at N.T.P.

1 g.	of hydrogen	at N.T.P.	occupies	....11.2	litres
8 g.	" oxygen	"	"	.... 5.6	"
35.5 g.	" chlorine	"	"	....11.2	"
14 g.	" carbon monoxide	"	"	....11.2	"
4 g.	" methane	"	"	.... 5.6	"
36.5 g.	" hydrogen chloride	"	"	....22.4	"

The volumes occupied by these combining weights are very closely related, as they are all simple multiples of 5.6 litres. Now, as has been explained already in Section 68, the combining weights selected in the above column are not the only possible ones; any simple multiples of these might be selected. Evidently, however, it would be a great advantage to select such a multiple for each that the combining weight of each would occupy the same volume. If 2 grams were selected for hydrogen, its volume would occupy 22.4 litres, and if 32 grams, 71 grams, 28 grams, 16 grams, and 36.5 grams, were selected respectively for oxygen, chlorine, carbon monoxide, methane, and hydrogen chloride, then in every case a combining weight would occupy 22.4 litres at N.T.P., which would, therefore, be the unit volume in chemistry.

The fact that hydrogen has been found to be the lightest of the elements led Cannizzaro to select the volume of 2 grams of it, measured at 0°C. and 760 mm. pressure, as the unit volume in chemistry.

At the present time, we select a unit volume which is in effect almost the same as the one selected by Cannizzaro in 1858, namely, the volume of 32 grams of oxygen measured at 0°C. and 760 mm. pressure. This volume is 22.4 litres or 22400 c.c., and the weight of this unit volume of any gaseous pure substance at 0°C. and 760 mm. pressure is called its *molecular weight.* Later in this book a more general meaning is given to this term.

Hence the weights of this volume of all gaseous pure substances will represent their combining weights, and the molecular weight of a substance is always one of the combining weights of that substance.

72. Finding of molecular weights.—The molecular weight can be determined by various experiments. A flask of known volume may be exhausted and weighed, and then filled with a gas, and weighed again. Or we may take a test-tube containing potassium chlorate, weigh it, and then heat it, and collect all the gas that is driven off (Fig. 3). If the test-tube is then weighed again, the difference will determine the weight of the oxygen collected, and if then the volume of gas is measured and the temperature and pressure recorded, we have all the data necessary for computing the molecular weight. Let us suppose that in the experiment described above we found 0.303 grams of oxygen to occupy 227 c.c., at 15°C. and 750 mm. pressure, then

0.303 g. at 15°C. and 750 mm. occupy .... 227 c.c.
0.303 g. at 0°C. and 760 mm. " $227 \times \frac{273}{288} \times \frac{750}{760}$ c.c.
$= 212.3$ c.c.
212.3 c.c. at N.T.P. weighs .... 0.303 g.
22400 c.c. " " " $0.303 \times \frac{22400}{212.3}$ g.
$= 32$ g.

The molecular weight of oxygen, therefore, is 32 grams. But in finding the molecular weight of a pure substance, it is not necessary that it should be gaseous at ordinary temperatures; for, since all gases expand equally for equal changes of temperature, the volume of the substance at any temperature can be reduced to normal conditions of temperature and pressure, and the molecular weight can then be obtained. Steam, for example, cannot be obtained at 0°C., yet we know that its molecular weight is 18 grams; for, if 22.4 litres of oxygen measured at 0°C. were heated to 100°C., and its volume measured, and if an equal volume of steam at the same temperature and pressure were then weighed, it would weigh 18 grams.

We conclude, therefore, that the molecular weight of any gaseous pure substance is the weight of a volume of it at any temperature and pressure equal to the volume occupied by 32 grams of oxygen at the same temperature and pressure.

73. Atomic weights.—The law of combining weights states that all pure substances react in the proportion of simple multiples of their reacting weights. If a combining weight of any one substance in a reaction is used, then the amounts of any others present in the reactions must be their combining weights. This is the case, also, when two or more elements unite in amounts which form the molecular weight of a compound. Since the molecular weight of the compound is one of its combining weights, the amounts of the constituents which are reacting must also be their combining weights. In other words, the molecular weight of any compound contains simple multiples of the reacting weights of its constituents. Let us tabulate some quantitative facts concerning some gaseous pure substances whose molecular weights can be found:

Name of substance	Molecular weight	Weight of constituents in a molecular weight				Molecular formula
		Carbon	Oxygen	Hydrogen	Chlorine	
Water	18		16	2		H_2O
Hydrogen chloride	36.5			1	35.5	HCl
Methyl chloride	50.5	12		3	35.5	CH_3Cl
Marsh gas	16	12		4		CH_4
Carbon tetrachloride	154	12			142	CCl_4
Carbon monoxide	28	12	16			CO
Carbon dioxide	44	12	32			CO_2
Carbonyl chloride	99	12	16		71	$COCl_2$
Chlorine dioxide	67.5		32		35.5	ClO_2
Oxygen	32		32			O_2
Hydrogen	2			2		H_2
Ozone	48		48			O_3
Hydrogen peroxide	34		32	2		H_2O_2
Acetylene	26	24		2		C_2H_2
Ethylene	28	24		4		C_2H_4
Formaldehyde	30	12	16	2		CH_2O
Acetic acid	60	24	32	4		$C_2H_4O_2$
Chloroform	119.5	12		1	106.5	$CHCl_3$

The pure substances in the above table are confined to those which contain the constituents carbon, hydrogen, oxygen, or chlorine. The second column contains the molecular weight of each, ascertained by weighing a measured volume of the gas, using the method illustrated for oxygen (Sec. 27). The adjacent columns contain the weights of the constituents in the molecular weights of the substances. The method of obtaining these weights of the constituents can be best explained by an illustration. If for that purpose, formaldehyde, the sixteenth substance in the list, is analysed, its composition is found to be

6.67 per cent. hydrogen,
53.33 per cent. oxygen,
40.00 per cent. carbon.

In a molecular weight (30 grams) there are, therefore,

$$\frac{6.67}{100} \text{ of } \frac{30}{1} = 2 \text{ grams hydrogen,}$$
$$\frac{53.33}{100} \text{ of } \frac{30}{1} = 16 \text{ grams oxygen,}$$
$$\text{and } \frac{40}{100} \text{ of } \frac{30}{1} = 12 \text{ grams carbon.}$$

The significance of the last column in the table on page 110 will be explained later.

The smallest amount of carbon present in a molecular weight of any of the substances in the table on page 110 is 12 grams, and the other amounts present are simple multiples of this. A like statement is true about the other constituents. The least amount of hydrogen is 1 gram, of oxygen 16 grams, and of chlorine 35.5 grams; the larger amounts of these elements are always simple multiples of these least amounts. The above list contains only a fraction of the pure substances which contain these constituents, and which are convertible into vapours, and hence whose molecular weight can be found. If, however, the full list were tabulated, no molecular weight of any of the pure substances would be found to have smaller weights of these elements than are found in the above table. Such weights as these are called *atomic weights*. The atomic weight of an element may, therefore, be defined as *the smallest weight of the element that is found in a molecular weight of any pure gaseous substance of which it is a constituent.* In order, therefore, to find the atomic weight of an element, it is necessary to analyse all pure substances of known molecular weight that contain it as a constituent; then to calculate the weight of the element in a molecular weight of each pure substance. The least weight that occurs is the atomic weight.

74. Why were 22.4 litres selected as the unit volume?—We are now prepared to answer this question. As has been explained in Section 71 the unit volume was selected which contained exactly a combining weight of oxygen, and hence of all other substances. The possible combining weights of oxygen are 8 grams, 16 grams, 32 grams, etc. If the volume of 16 grams had been selected as the unit volume, instead of 32 grams, then the molecular weight of oxygen would have been 16 grams; and the molecular weight of all the substances in the foregoing list would have been halved. This would make the atomic weight of hydrogen 0.5 grams. But, for evident reasons, Cannizzaro desired to represent the smallest atomic weight by unity, and, accordingly, selected 22.4 litres as the unit volume. Thus hydrogen, the element with the lowest atomic weight, had unity for its atomic weight. For reference, a list of the common elements with their exact atomic weights is printed on the inside back cover of this volume.

75. The selection of possible combining weights.— In Section 68 it is stated that there are various possible combining weights for each pure substance, any one of which might be selected. We are now in a position to make a final selection of the most suitable combining weights. Its atomic weight is the one that is always selected for each element, and its molecular weight for each compound. These are what we have called the reacting weights.

76. Symbols and formulæ.—

> "Such symbolic representations have been in vogue in chemistry from the earliest times, when the metals in particular obtained the signs of the planets. . . With the discovery of the law of combining weights, however, these symbolic representations received an extended, quantitative meaning, as they then had to represent a combining weight of the substance in question."
>
> —*William Ostwald*

In chemical reactions it is necessary to express concisely the exact quantities of the reacting substances. Various attempts were made to do this by means of symbols.

Dalton used a different sign for each element; and combinations of these signs expressed the composition of compounds. In Figure 29 we show some of his symbols; and also how they were combined to express the composition of compounds. Dalton's symbols, however, being cumbersome, were soon abandoned for those of Berzelius, which have been in common use ever since. According to his method of representation we let

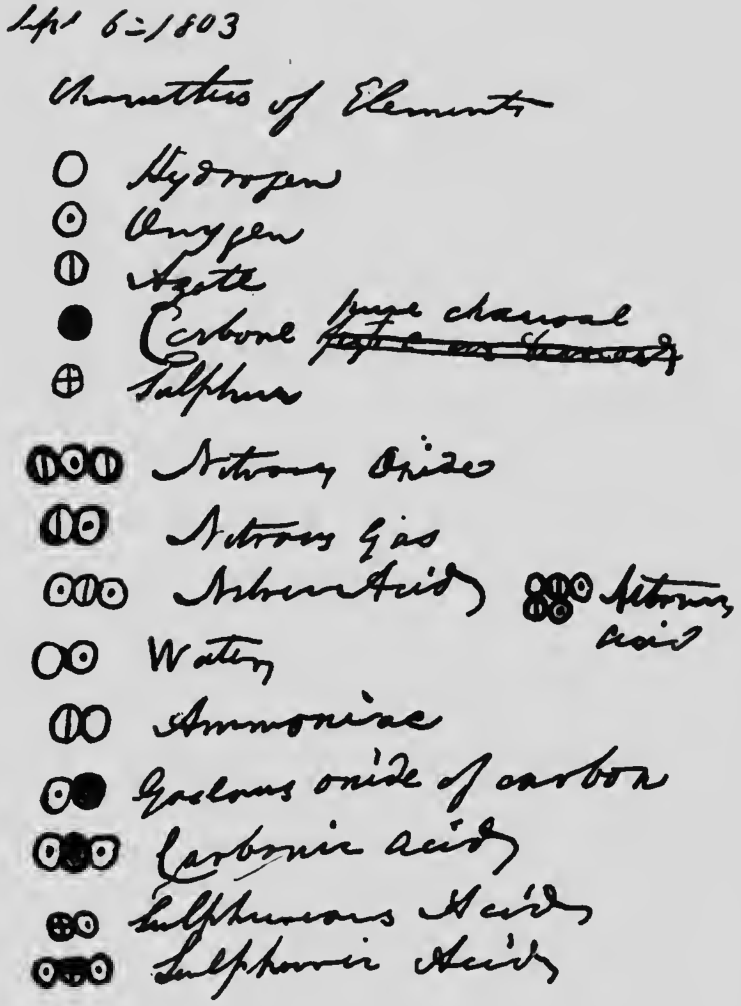
O stand for the atomic weight of oxygen, 16 grams,

Cl stand for the atomic weight of chlorine, 35.5 grams,

C stand for the atomic weight of carbon, 12 grams,

H stand for the atomic weight of hydrogen, 1 gram;

and all the other elements have symbols expressing their atomic weights. Usually the first letter of the element is used as the symbol, as B for boron, and C for carbon. Where several elements begin with the same letter, two letters are used, a capital followed by a small letter, as Ca for calcium, Cl for chlorine, and Co for cobalt. It is evidently more convenient that symbols should be the same in all languages; hence the first letter or letters of the Latin name are generally used, as, Fe (Lat. *ferrum*) for iron; Cu (Lat. *cuprum*) for copper; Pb (Lat. *plumbum*) for lead; K (Lat. *kalium*) for potassium; Na (Lat. *natrium*) for sodium. And it cannot be emphasized too strongly that these symbols are not mere abbreviations standing for the names of the elements; they also always stand for a definite weight of the element, namely, the atomic weight. For the convenience of pupils, on the inside of the back cover of this volume is given a list of the common elements, their symbols, and their atomic weights, as fixed by an international committee who have investigated and chosen the most accurate number, and in the next column, the approximate atomic weights.



Sept 6 = 1803

Characters of Elements

Hydrogen

Oxygen

Azote

Carbone pure charcoal ~~[illegible]~~

Sulphur

Nitrous Oxide

Nitrous Gas

Nitric Acid

Nitrous acid

Water

Ammoniac

Gaseous oxide of carbon

Carbonic acid

Sulphurous Acid

Sulphuric Acid

FIG. 29.—FACSIMILE FROM DALTON'S NOTE-BOOK SHOWING HIS ORIGINAL SYMBOLS GIVEN TO THE ELEMENTS, AND HIS METHOD OF COMBINING THEM TO EXPRESS THE COMPOSITION OF COMPOUNDS

Azote = nitrogen
Nitrous gas = nitric oxide
Nitric acid = nitrogen peroxide
Nitrous acid = nitrogen trioxide
Gaseous oxide of carbon = carbon monoxide
Sulphurous acid = sulphur dioxide
Sulphuric acid = sulphur trioxide.

The molecular weight of water, (see list on page 110), contains 2 grams of hydrogen (two atomic weights), and 16 grams of oxygen (one atomic weight). Its composition could be expressed by the combination of symbols HHO, each H standing for 1 gram of hydrogen and the O standing for 16 grams of oxygen. But instead of repeating each symbol for each occurrence of its atomic weight in a molecular weight of the substance, we put a numerical index below it; thus H_2O. Such a group of symbols expressing the composition of a pure substance is called a *formula*, and when the formula expresses the composition of a molecular weight, as in the case of H_2O, it is called a *molecular formula*. The molecular formula of each substance in the list on page 110 is written in the last column, and these should be studied carefully. Take the case of carbon dioxide:

CO_2 is the molecular formula for carbon dioxide. Let us see what a large amount of definite information is packed into the brief space of this group of symbols. It expresses the following facts:

(1) That a molecular weight of carbon dioxide contains 12 grams of carbon and 32 grams of oxygen;

(2) that 22.4 litres of carbon dioxide at 0°C. and 760 mm. pressure weigh 44 grams;

(3) that 44 grams of carbon dioxide, or a simple multiple of it, always reacts with a combining weight of any other pure substance;

(4) that CO_2 stands for 44 grams.

To find the formula of a pure substance it is necessary to know its constituents, and the proportions in which these constituents are present in the substance. Suppose a gas has been analysed and found to contain 85.73 per cent. of carbon, and 14.28 per cent. of hydrogen, and we desire to find its formula. We know that the constituents are present in the proportion of their atomic weights, or of simple multiples of them. If we select 1 atomic weight of carbon and find the quantity of hydrogen that is united with it, we are quite certain that this amount must be 1 gram, (its atomic weight), or some simple multiple of its atomic weight.

In the above example:

85.73 grams of carbon are combined with 14.28 grams of hydrogen;

1 gram of carbon is combined with $\frac{14.28}{85.73}$ grams of hydrogen;

12 grams of carbon are combined with $\frac{14.28}{85.73}\times\frac{12}{1}=2$ grams of hydrogen;

12 grams of carbon are represented by C, 2 grams of hydrogen are represented by H_2.

The simplest formula, therefore, is CH_2; but the formula might as well be written C_2H_4, C_3H_6, etc., for all of these have the above percentage composition. But as a molecular formula always represents the weight of 22.4 litres of the substance in the form of a gas, in order to decide which of the above is the molecular formula, it is necessary to know the density of the substance in the form of a gas. If, then, we also know that 1 litre of the gas at 0°C. and 760 mm. pressure weighs 1.25 grams, we are able to determine which of these formulæ is the correct one: 22.4 litres of the gas at the normal temperature and pressure weigh 1.25 grams × 22.4 = 28 grams.

CH_2 represents a weight of $12+2=14$ grams,

C_2H_4 represents a weight of $24+4=28$ grams,

C_3H_6 represents a weight of $36+6=42$ grams; hence the molecular formula is C_2H_4.

Example 1. A substance on analysis gives the following composition: hydrogen, 1.59 per cent.; nitrogen, 22.22 per cent.; oxygen, 76.19 per cent. One litre of the substance in the form of a gas at 90°C. and 700 mm. pressure weighs 1.95 grams. Find its molecular formula.

1 litre at 90°C. and 700 mm. pressure would occupy

$1 \times \frac{273}{363} \times \frac{700}{760}$ litres at N.T.P.

$1 \times \frac{273}{363} \times \frac{700}{760}$ litres at N.T.P. weighs . . . . 1.95 g.

22.4 " " " " $1.95 \times \frac{363}{273} \times \frac{760}{700} \times 22.4$ g.

= 63 g.

1.59 g. hydrogen combines with 22.22 g. nitrogen and 76.19 g. oxygen.

1 g. " " " $\frac{22.22}{1.59}$ g. " " $\frac{76.19}{1.59}$ g. "

= 13.98 g. " " 47.92 g. "

13.98 grams of nitrogen is approximately N, and 47.92 grams of oxygen is approximately O_3, hence the simplest formula is HNO_3. The molecular weight of a substance of this formula is H, 1 gram,

N, 14 grams,
O_3, 48 grams,
―
63 grams.

But we found above that the molecular weight was 63 grams; therefore HNO_3 is the correct molecular formula.

Example 2. If 1.23 grams of aluminium are burned in oxygen, and the resulting oxide weighs 2.32 grams, find the simplest formula for aluminium oxide.

1.23 grams of aluminium combine with (2.32 − 1.23) grams = 1.09 grams oxygen.

27 grams of aluminium combine with 1.09 grams $\times \frac{27}{1.23} =$ 23.9 grams.

$\frac{23.9}{16} = 1\frac{1}{2}$ atomic weights of oxygen.

Therefore the simplest formula is $AlO_{1\frac{1}{2}}$, or Al_2O_3, as no fraction of an atomic weight is ever used in a formula.

QUESTIONS

1. The weight of 1 litre of a gas at 0°C. and 760 mm. pressure is 5.236 grams. Find its molecular weight.

2. The formula of hydrogen is H_2. What is the weight of 1 litre of hydrogen, measured at normal temperature and pressure?

3. A bottle full of air weighs 101.446 grams; when filled with sulphur dioxide it weighs 101.837 grams; when filled with water it weighs 351.123 grams. If 1 litre of air weighs 1.293 grams, find the molecular weight of sulphur dioxide.

4. Sulphur dioxide contains 50 per cent. of oxygen and 50 per cent. of sulphur. Find its molecular formula. (See question 3 for its molecular weight.)

5. The molecular weight of cyanogen is 52 grams. What is its density as compared with air? (Sec. 24) What is the weight of 1 litre of it at 0°C. and 760 mm. pressure? It contains 46.08 per cent. carbon and 53.92 per cent. nitrogen. What is its molecular formula?

6. Hydrogen sulphide, H_2S,
Nitric oxide, NO,
Ammonia, NH_3,
Marsh gas, CH_4,
Methyl Chloride, CH_3Cl.

For each of the above substances find (*a*) the molecular weight; (*b*) the percentage composition; (*c*) the weight of 1 litre of the gas at N.T.P.; (*d*) how many times it, as a gas, is as heavy as air (density compared with air); (*e*) the number of times it is as heavy as hydrogen (density compared with hydrogen); (*f*) the volume of 1 gram at N.T.P.

7. What weight of oxygen could be obtained from 200 grams of mercuric oxide, HgO?

8. One litre of oxygen at 0°C. and 760 mm. pressure weighs 1.429 grams. What is its molecular weight?

9. 1c.c. of sulphur dioxide at N.T.P. weighs 0.000286 grams. Calculate its molecular weight.

10. What weight does each of the following represent: O_3, NH_3, H_2SO_4, N_2, Hg, H_2O, $KClO_3$?

11. If one gram of liquid ozone were to evaporate, what volume would it occupy under N.T.P., if it all remained as gaseous ozone, whose formula is O_3? If 90 per cent. were converted into oxygen gas, O_2, in evaporating, what volume would the mixture of oxygen and ozone occupy?

12. Calculate the simplest formulæ of the compounds which have the following percentage composition, (correct to the second decimal)

(*a*) Chlorine, 60.68; sodium, 39.31.
(*b*) Sulphur, 23.52; calcium, 29.41; oxygen, 47.05.
(*c*) Carbon, 40; hydrogen, 6.67; oxygen, 53.33.
(*d*) Nitrogen, 26.17; hydrogen, 7.48; chlorine, 66.35.

13. Calculate the simplest formulæ of the following compounds: (*a*) 18 grams of the substance contains 8.4 grams of iron and 9.6 grams of sulphur. (*b*) 0.84 grams of the substance contains 0.587 grams of iron and 0.253 grams of oxygen.

14. Ether contains 64.86 per cent. carbon, 13.51 per cent. hydrogen, and 21.62 per cent. oxygen. One litre of the ether at 100°C. and 760 mm. pressure weighs 2.42 grams. Calculate the molecular formula.

15. A substance contains 29 per cent. sodium, 40.5 per cent. sulphur, and 30.5 per cent. oxygen. Its molecular weight is 158 grams. Calculate its molecular formula.

16. A substance contains 80 per cent. carbon, and 20 per cent. hydrogen. Its vapour is fifteen times as heavy as hydrogen. Calculate its formula.

17. It has been found that 3 grams of carbon unite with 8 grams of oxygen to form an oxide of carbon. What is the simplest formula of the oxide?

18. Morley found that 1.429 grams of oxygen were contained in 1 litre at N.T.P., and that 0.08987 grams of hydrogen were contained in 1 litre. Lord Rayleigh found that 1.2505 grams of nitrogen were contained in 1 litre at N.T.P. Calculate the molecular weights of these three elements.

19. A glass globe full of air at 0°C. and 760 mm. weighs 51.125 grams. The glass globe full of stannic chloride gas at 150°C. and 760 mm. weighs 52.682 grams. The volume of the globe is 250 c.c. From the above data find the molecular weight of stannic chloride.

20.

	Molecular weight			
Carbon chloride...	154	Carbon 7.8%	Chlorine, 92.2%	
Chloroform.......	119.5	Carbon 10.06%	Hydrogen, 0.84%	Chlorine, 89.2%
Phosphorus chloride........	137.5	Phosphorus, 22.57%	Chlorine, 77.43%	
Sulphuryl chloride.	135	Sulphur, 23.72%	Oxygen, 23.72%	Chlorine, 52.56%
Hydrogen chloride	36.5	Chlorine, 97.26%	Hydrogen, 2.74%	

If the foregoing were the only gaseous pure substances containing chlorine, from the data given find the atomic weight of chlorine.

21. Deduce the formula of alcohol from the following data concerning it: Its percentage composition is carbon 52.17 per cent.; hydrogen, 13.04 per cent.; oxygen, 34.80 per cent.; its vapour density is 1.59 (air=1).

22. Cane sugar contains carbon, hydrogen, and oxygen only. .30 grams of it when completely burnt in air to water and carbon dioxide gave 0.463 grams of the latter and 0.174 grams of the former. The formula of carbon dioxide is CO_2, of water H_2O. The molecular weight of sugar is 342. Find its formula.

CHAPTER IX

EQUATIONS, VALENCY, AND NOMENCLATURE

77. Chemical equations.—In the last chapter it was shown that much information regarding a pure substance can be expressed by combining the symbols of its constituents into a suitable formula. The formula, however, does not mark the limit of this condensed form of expressing chemical facts. We will now show how, by various combinations, we can represent concisely the qualitative and quantitative relationships of all the pure substances taking part in a reaction:

If 1 gram of magnesium is heated in air, it unites with 0.656 grams of the oxygen of the air to produce 1.656 grams of magnesium oxide. Therefore 24.4 grams of magnesium, (one atomic weight), unites with 0.656 grams×24.4 =16 grams of oxygen (one atomic weight) to produce 1.656 grams×24.4=40.4 grams of magnesium oxide. We thus see that the simplest formula of magnesium oxide is MgO.

The above facts might be expressed thus:

$$Mg+O \longrightarrow MgO.$$

This would be read thus: 24.4 grams of magnesium react with 16 grams of oxygen to produce 40.4 grams of magnesium oxide, (the sign + on the left side standing for "reacts with" and ⟶ stands for "to produce"). Such a combination of formulæ is called a *chemical equation.* But whenever we have the molecular formula (as we have for all gases), only that formula is used in equations; we never write O for gaseous oxygen, as we have found that the weight of 22.4 litres of this element is 32 grams and its molecular formula is therefore O_2. Hence the foregoing equation should be written:

$$2Mg+O_2 \rightarrow 2MgO.$$

We do not write the formula of magnesium Mg_2, because that would represent a pure substance whose molecular weight is 48.8 grams, and up to the present time the molecular weight of magnesium has not been determined by chemists. Where the substance is not a gas, we write the formula as simply as possible, as in MgO, and the weight expressed by it is called the *formula weight*, as it would not be correct to call it the molecular weight. A number before the formula, like the 2 before Mg and before MgO, indicates that twice the formula weight is taken.

When 4 grams of hydrogen unite with 32 grams of oxygen, 36 grams of steam are produced. The equation expressing this is written as follows:

$$2H_2+O_2 \rightarrow 2H_2O,$$

because quantitative investigations have shown that H_2, O_2, H_2O are the molecular formulæ of the three substances occurring. Accordingly, $2H_2$ stands for the 4 grams of hydrogen, O_2 for the 32 grams of oxygen, and $2H_2O$ for the 36 grams of steam.

To write an equation it is necessary, therefore, to have the following information:

(1) The formulæ of all the substances taking part in the reaction. (2) The proportions in which they react. If, however, the formulæ of the substances reacting are known, the probable equation can generally be worked out without actually weighing each substance in the reaction. We will now illustrate how this is done.

78. Writing equations.—Before writing equations, the pupil must know the composition of all the substances taking part in the reaction, both before and after the chemical change. The formulæ of these he will either know or find from a book. The method described in Sections 86 and 87 shows how the formulæ of most of the substances used in elementary chemistry can be written without taxing the mind with actually memorizing them. It is, then, necessary only to remember the law of the conservation of the elements (Sec. 33), in order to know that there must be as many atomic weights of each element on one side of the equation as on the other. The requisite number of molecular weights of each substance must be taken to produce the above equality of atomic weights on each side of the equation, and fractional parts of a molecular weight are usually avoided. The estimating of the proper number of molecular weights of each substance is called *balancing the equation*. Let us take an example: When potassium chlorate is heated strongly, it is decomposed into potassium chloride and oxygen. The formula of potassium chlorate is $KClO_3$; that of oxygen O_2, and that of potassium chloride KCl. The first attempt at the equation is

$$KClO_3 \longrightarrow KCl + O_2.$$

But there are three atomic weights of oxygen on the left, and only two on the right. If 1½ molecular weights of oxygen were placed on the right, the equation would balance thus:

$$KClO_3 \longrightarrow KCl + 1\tfrac{1}{2}O_2.$$

But as fractions are usually avoided, we multiply throughout by 2, which gives us the final equation:

$$2KClO_3 \longrightarrow 2KCl + 3O_2.$$

Several other points should be noted about equations. The method just described of writing equations is merely a device to assist the chemist. The real method by which an equation is first written is that described for the reaction in which magnesium is burned in air, where the quantities of all the substances are determined (see page 122). Again, the fact that a balanced equation can be written to express a reaction is no indication that the reaction will take place. Equations are solely for expressing the results of reactions; the equation merely expresses the quantitative relations of the substances involved, and tells nothing about the conditions under which the reaction takes place, such as whether the substances were hot or cold, whether in water or in air, and whether they were decomposed by electricity, heat, or light.

The following are the equations of some of the more important reactions that have been discussed in the earlier chapters of this volume; each should be carefully studied in relation to the experiment as described in the text-book:

Heating substances in air or oxygen, Chapters 1 and 2;

$$\begin{aligned} 3Fe + 2O_2 &\longrightarrow Fe_3O_4, \\ 2Zn + O_2 &\longrightarrow 2ZnO, \\ Sn + O_2 &\longrightarrow SnO_2, \\ 2Hg + O_2 &\longrightarrow 2HgO, \\ 4P + 5O_2 &\longrightarrow 2P_2O_5. \end{aligned}$$

Preparing oxygen from sodium peroxide (Sec. 15);

$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2.$$

Heating magnesium in nitrogen (Sec. 19);

$$3Mg + N_2 \longrightarrow Mg_3N_2.$$

Preparing nitrogen from ammonium chloride and sodium nitrite (Sec. 20);

$$NH_4Cl + NaNO_2 \longrightarrow NaCl + N_2 + 2H_2O.$$

Preparation of hydrogen, Chapter 4;

$$2Na+2H_2O \longrightarrow H_2+2NaOH,$$
$$Mg+H_2O \longrightarrow MgO+H_2,$$
$$3Fe+4H_2O \longrightarrow Fe_3O_4+4H_2,$$
$$H_2SO_4+Zn \longrightarrow ZnSO_4+H_2.$$

79. Quantitative meaning of equations.—

$$2H_2+O_2 \longrightarrow 2H_2O.$$

This equation conveys the following information: (1) That 4 grams of hydrogen combine with 32 grams of oxygen to produce 36 grams of steam; and (2) that 44.8 litres (the volume of 2 molecular weights) of hydrogen combine with 22.4 litres (the volume of 1 molecular weight) of oxygen to produce 36 grams of water, the gases being measured at N.T.P. Hence we can say that 2 volumes of hydrogen combine with 1 volume of oxygen at any temperature and pressure to produce water. If the temperature and pressure are such that the water appears as steam, the equation tells us that 2 volumes of hydrogen combine with 1 volume of oxygen to produce 2 volumes of steam. A molecular formula, accordingly, stands for both a molecular weight and a molecular volume, and whichever is more useful for the purpose under consideration is selected.

80. Chemical arithmetic.—

Example 1. When zinc acts on sulphuric acid to produce zinc sulphate and hydrogen, the equation for the reaction is

$$Zn+H_2SO_4 \longrightarrow ZnSO_4+H_2.$$

If 12 grams of zinc are used, how many grams of sulphuric acid are necessary to act on it completely, what weight of zinc sulphate is formed, and what volume of hydrogen is liberated, measured at N.T.P.?

$$\begin{array}{ccccccc}
\text{Zn} & + & H_2SO_4 & \longrightarrow & ZnSO_4 & + & H_2 \\
65.4\text{ g.} & + & \left\{\begin{array}{l} H_2 = 2\text{ g.} \\ S = 32\text{ g.} \\ O_4 = 64\text{ g.} \end{array}\right\} & \text{gives} & \left\{\begin{array}{l} Zn = 65.4\text{ g.} \\ S = 32\text{ g.} \\ O_4 = 64\text{ g.} \end{array}\right\} & + & \begin{array}{c} 2\text{ g.} \\ (22.4\text{ litres}) \end{array} \\
\text{Zn} & & H_2SO_4 & & Zn\,SO_4 & & H_2 \\
65.4\text{ g.} & + & 98\text{ g.} & \text{gives} & 161.4\text{ g.} & + & 2\text{ g.}
\end{array}$$

1st. To find what weight of sulphuric acid is necessary.

65.4 grams of zinc require 98 grams sulphuric acid.

12 grams of zinc require 98 grams $\times \frac{12}{65.4} = 17.98$ grams.

2nd. To find the weight of zinc sulphate produced.

65.4 grams of zinc produce 161.4 grams of zinc sulphate.

12 grams of zinc produce 161.4 grams $\times \frac{12}{65.4} = 29.61$ grams.

3rd. To find the volume of hydrogen at N.T.P. produced.

65.4 grams of zinc when acting on sulphuric acid produce 22.4 litres of hydrogen at N.T.P.

12 grams of zinc produce 22.4 litres $\times \frac{12}{65.4} = 4.11$ litres at N.T.P.

Example 2. A balloon of 1,500 litres capacity is filled with hydrogen, which has been produced by the action of sulphuric acid on zinc. If the hydrogen in the balloon is at 800 mm. pressure when at a temperature of 20° C., what weight of zinc was used in generating the gas?

At 1800 mm. and 20°C. volume is . . . . 1500 l.

" 760 " " 0°C. " " . $1500 \times \frac{273}{293} \times \frac{800}{760}$ l.

= 1471 l.

From equation in Example 1

22.4 l. hydrogen at N.T.P. require . . . . . . 65.4 g. zinc.

3310 l. " " " " $65.4 \times \frac{1471}{22.4}$ g. "

= 4296 g. zinc.

Example 3. 200 litres of hydrogen are mixed with 150 litres of oxygen, and the two are exploded. (*a*) If the gases both before and after the explosion are measured at 0° C. and 760 mm. pressure, what volume of gas will there be after the explosion? (*b*) If the gases are measured at 100° C. and 760 mm. pressure what volume will the gases occupy after the explosion?

(*a*) $2H_2+O_2 \longrightarrow 2H_2O$.

At N.T.P. 2 volumes of hydrogen + 1 volume of oxygen produce liquid water at N.T.P.

200 litres of hydrogen + 100 litres of oxygen produce liquid water.

So there will be (150 − 100) litres = 50 litres of unused oxygen.

(*b*) At 100° C. and 760 mm. 2 vol. of hydrogen + 1 vol. oxygen produce 2 vol. steam.

At 100° C. and 760 mm. 200 litres of hydrogen + 100 litres of oxygen produce 200 litres of steam.

So the gas after explosion will consist of 50 litres of oxygen + 200 litres of steam, or a total of 250 litres.

81. Valency.—The methods of finding the composition of pure substances, such as mercuric oxide and magnesium oxide, have been already studied (see Sec. 35). We have also learned how the composition of such substances can be represented by formulæ. In the following table the composition of a number of compounds of hydrogen with another element are expressed by formulæ:

HCl	H_2O	HN_3	CH_4
HBr	H_2S	PH_3	SiH_4
HI	H_2Ca	SbH_3	

From the law of combining weights we know that 35.5 grams of chlorine (Cl), 14 grams of nitrogen (N) or 12 grams of carbon (C) unite with 1 gram of hydrogen (H), or some simple multiple of 1 gram (H, H_2, H_3, etc.); but up to the present we have no method of predicting with which multiple of the atomic weight of hydrogen one atomic weight of the other elements will combine. It will be noticed from the formulæ before listed that one atomic weight of chlorine, bromine, or iodine combines with *one* atomic weight of hydrogen; that one atomic weight of oxygen or sulphur combines with *two* atomic weights of hydrogen; that one atomic weight of nitrogen, phosphorus, arsenic, or antimony combines with *three* atomic weights of hydrogen; and that one atomic weight of carbon or silicon combines with *four* atomic weights of hydrogen. The elements can be classified according to the number of atomic weights of hydrogen with which an atomic weight of each combines. Those, like chlorine, bromine, and iodine, that combine with one atomic weight of hydrogen are *univalent;* oxygen and sulphur are *bivalent;* nitrogen, phosphorus, etc. are *trivalent;* and carbon and silicon are *quadrivalent.*

To express the number of atomic weights of hydrogen that combine with one atomic weight of any element the word *valency* is used.

Now there is a very simple natural law connecting valency and the proportions in which elements react. This can be illustrated by a few examples: If phosphorus (trivalent) combines with oxygen (bivalent) it does so in the proportion expressed by the formula, P_2O_3, and it will be noticed that the number of atomic weights of each element are in the inverse proportion of their valencies. Again, antimony (trivalent) combines with chlorine (univalent) in the proportion expressed by the formula, $SbCl_3$, namely 1 to 3, being likewise the inverse proportion of the valencies, 3 to 1. Further, if calcium hydride is converted into calcium oxide, one atomic weight of oxygen (bivalent) has replaced two atomic weights of hydrogen (univalent), in which again the numbers are in the inverse proportion of the valencies. The natural law referred to above may consequently be stated as follows: *The numbers of atomic weights of elements reacting are inversely as their valencies.* This law, although not so widely applicable as the law of combining weights, is very useful as an aid in remembering and even in predicting formulæ (Sec. 88).

Although the valency of the elements was stated above to be the number of atomic weights of hydrogen that combine with one atomic weight of those elements, the valency law just illustrated affords a method of finding the valencies of elements that do not combine with hydrogen. For example, aluminium, whose hydride is difficult to prepare, combines easily with chlorine, forming the substance whose formula is $AlCl_3$. If the proportion 1 to 3 is the inverse ratio of the valencies of aluminium and chlorine, and chlorine as defined above is univalent, clearly aluminium must be trivalent.

82. Different valencies of the same element.—The law of multiple proportions indicates that two elements may combine in different proportions. Sulphur forms two oxides whose formulæ are SO_2 and SO_3. In the first, sulphur is quadrivalent, in the second it is sexivalent. Mercury forms two chlorides, $HgCl_2$ and $HgCl$; as chlorine is univalent, mercury is univalent and bivalent.

In the table at the top of page 130 is given a list of common elements classified according to their valencies. Some, it will be seen, have more than one valency and are placed in two or more columns.

83. Determination of valency.—In accordance with what has been said above, we may determine experimentally the valency of an element by finding how it combines with or replaces another element whose valency is known. The following experiment shows how to find

VALENCY OF THE ELEMENTS

Univalent	Bivalent	Trivalent	Quadrivalent	Quinquivalent	Sexivalent
Bromine	Barium	Aluminium	Carbon	Antimony	Sulphur
Chlorine	Calcium	Antimony	Lead	Arsenic	
Hydrogen	Copper	Arsenic	Manganese	Bismuth	
Iodine	Iron	Bismuth	Sulphur	Nitrogen	
Mercury	Lead	Iron	Tin	Phosphorus	
Potassium	Magnesium	Nitrogen			
Silver	Manganese	Phosphorus			
Sodium	Mercury				
	Oxygen				
	Strontium				
	Sulphur				
	Tin				
	Zinc				

the valency of zinc and other metals. If apparatus is prepared like that illustrated in Figure 30, a metal may be placed in the test-tube, and by adding a suitable acid, the hydrogen that is liberated can be collected in the bottle and its volume readily measured. Suppose we put 1.04 grams of zinc into the test-tube. The volume of gas collected in the bottle is 387.40 c.c. measured at 20° C. and 750 mm. pressure. The volume of hydrogen liberated from the acid by the zinc was 387.40 c.c.; for, though the test-tube and connections were full of air at the beginning and are now filled with hydrogen, the volume of gas in the bottle measures the increase in the total volume of gas, and this increase was entirely due to the generation of the hydrogen; thus

1.04 grams of zinc displace 387.40 c.c. of hydrogen at 20° C. and 750 mm.

1.04 grams of zinc displace 387.40 c.c. $\times\frac{273}{293}\times\frac{750}{760}$ of hydrogen at N.T.P.

65.4 grams of zinc displace 387.4 c.c.$\times\frac{273}{293}\times\frac{750}{760}\times\frac{65.4}{1.04}=$ 22400 c.c.,
or 1 atomic weight of zinc displaces 2 atomic weights of hydrogen, for 22400 c.c. is 22.4 litres, which is the volume of 2 grams of hydrogen. Therefore zinc is bivalent.

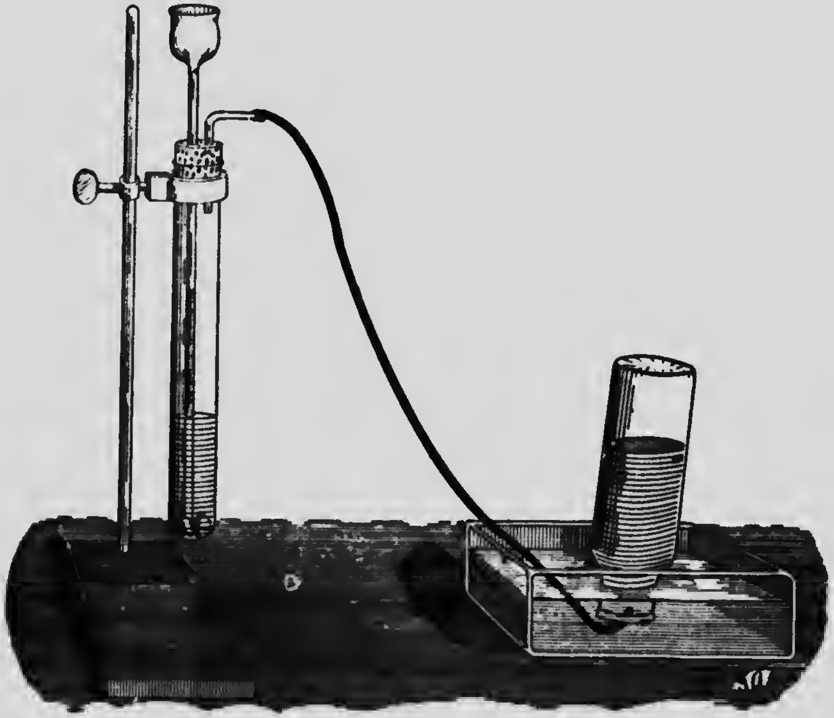


Fig. 30.—Apparatus for Measuring the Volume of Hydrogen Displaced by Metals

84. Radicles.—Sulphuric acid, when copper is added to it, produces copper sulphate. When this is acted on by calcium chloride a white precipitate of calcium sulphate is produced; and, if some of this is dissolved in water and strontium chloride is added to it, a precipitate of strontium sulphate is formed, which, when dissolved in water, gives a precipitate of barium sulphate on the addition of barium chloride. Let us write down the formulæ of the substances formed in this series of reactions:

sulphuric acid	H_2SO_4,
copper sulphate	$CuSO_4$,
calcium sulphate	$CaSO_4$,
strontium sulphate	$SrSO_4$,
barium sulphate	$BaSO_4$.

It will be noted that the two constituents, sulphur and oxygen, in exactly the same proportion (32 grams of sulphur to 64 grams of oxygen), expressed by the symbols SO_4, are present in sulphuric acid and in each of the sulphates in the four successive reactions. *Such a group of elements that is present in a number of compounds and that passes through a number of reactions is called a radicle.* Nitric acid, HNO_3, phosphoric acid, H_3PO_4, carbonic acid, H_2CO_3, and potassium hydroxide, KOH, all have radicles, which are respectively NO_3, PO_4, CO_3, and OH. The foregoing radicles are each given a special name; SO_4 is the sulphate radicle; NO_3 the nitrate radicle; CO_3 the carbonate radicle; and OH the hydroxyl radicle. Valencies may be assigned to the radicles as well as to the elements, and the formulæ above will indicate clearly what the valency is for each. In HNO_3 the radicle NO_3 is combined with one atomic weight of hydrogen, and so it is univalent; SO_4 and CO_3 are bivalent, as they are each combined with two atomic weights of hydrogen; PO_4 is trivalent, and OH is univalent, as it is combined with an atomic weight of potassium, a univalent element. In the same way, the valency of other radicles can usually be determined by an inspection of formulæ containing them.

In writing formulæ containing radicles, it is well to express the formulæ so as to show at a glance the presence of the radicle. In calcium nitrate, calcium being bivalent, one atomic weight of it combines with two NO_3 radicles, so that the formula would be CaN_2O_6; but to indicate clearly the presence of the radicle we always write it $Ca(NO_3)_2$. The formula of aluminium nitrate is $Al(NO_3)_3$; of tin hydroxide $Sn(OH)_4$, not SnO_4H_4.

85. Nomenclature.—

> "Every physical science is formed, necessarily, of three things: the series of facts which constitute the science, the ideas which recall, and the words which express these facts. The word ought to call forth the idea, the idea depict the fact; they are three impressions of the same seal."
>
> —*Antoine Laurent Lavoisier, 1787*

Up to the time when the great Lavoisier wrote the above words, the naming of substances was unsystematic and often whimsical; frequently the names conveyed no indication of the composition or the relationship of the substances. Mercuric oxide was called *mercurius calcinatus per se*, if formed by heating mercury, and *red precipitate*, if formed by acting on mercury with nitric acid: such names as *vitriolated tartar*, *flowers of zinc*, *diaphoretic antimony*, *dephlogisticated air*, and *aethiops per se* adorned the pages of the books on chemistry; and, as new substances were continually being discovered, the names soon became a serious tax on the memory. To provide suitably for the requirements of chemistry as he defines them above, Lavoisier originated a scientific nomenclature, which forms the basis of the one we now use.

According to our present system, every substance composed of only two elements has a name ending in *-ide*, and this name is composed of the names of the two elements, the name of the metal being placed first and the second name being generally shortened: HgO, for example, is mercury oxide; PH_3 is hydrogen phosphide; and CuS is copper sulphide. Where an element has two valencies, it will frequently unite in two proportions with another element; then it has the suffix *-ous* in the substance in which it has the lower valency, but *-ic* in the one in which it has the higher valency: Mercury, for example, forms two chlorides, $HgCl$ and $HgCl_2$; the first is mercur*ous* chloride, the second is mercur*ic* chloride; As_2O_3 is arseni*ous* oxide, and As_2O_5 is arsen*ic* oxide. Frequently such substances are named in a different way and without much regularity; in such cases the names have to be memorized: CO and CO_2, for example, are usually called carbon monoxide and carbon dioxide, not carbonous oxide and carbonic oxide; but the exceptions to the general rule are usually confined to the oxides and will not be difficult to master.

86. Naming of oxygen acids.—All acids contain hydrogen, and most of those used in elementary chemistry contain oxygen and a third element, which varies in the different acids. These oxygen acids, as they are called, are usually in sets, each containing the three elements, and in each set only the amounts of oxygen vary. Here is one set:

$$HClO, \quad HClO_2, \quad HClO_3, \quad HClO_4.$$

Now in such a set the most common one, or the one first discovered—in this case $HClO_3$—is called chloric acid, this being the name of the distinguishing element, chlorine, (oxygen and hydrogen are common to all these acids) followed by the suffix *-ic*; and the names of all the members of the set are as follows:

$HClO$	*hypo*-chlor-*ous* acid,
$HClO_2$	chlor-*ous* acid,
$HClO_3$	chlor-*ic* acid,
$HClO_4$	*per*-chlor-*ic* acid.

For any other similar set of acids the syllable *chlor* has merely to be replaced by the suitable word depending on the characteristic element of the set. In every such set each member has one atomic weight of oxygen more than the one immediately preceding. If, accordingly, we know which member of the series is the *-ic* acid, the names of the others may be ascertained readily on reference to the names in the set. Now the names of the *-ic* acids in question are as follows:

chloric acid	$HClO_3$,
nitric acid	HNO_3,
carbonic acid	H_2CO_3,
sulphuric acid	H_2SO_4,
phosphoric acid	H_3PO_4.

The names and formulæ of these should be committed to memory, and then the formulæ of any other members of the sets can be at once written, and, on the other hand, if the formula is given, the acid can be named.

If the pupil is required to give a name to the acid whose formula is H_3PO_2, he writes first the formula of the corresponding *-ic* acid, which is H_3PO_4, and secondly the other members of the set, until the required member is reached. H_3PO_3 is phosphorous acid, and H_3PO_2 is hypophosphorous acid, the name required.

If the pupil is required to write the formula of a substance whose name is nitrous acid, he proceeds in a similar manner: Nitric acid is HNO_3; the next in the series is nitrous acid, whose formula is HNO_2., *hence to find the name or the formula always begin with the -ic acid.*

87. Naming salts of oxygen acids.—All the foregoing oxygen acids form salts by replacing the hydrogen with a metal. The salt is named by changing the suffix of the name of the acid from *-ous* to *-ite* and from *-ic* to *-ate*, and prefixing to it the name of the metal that replaces the hydrogen. Examples are given in the following table:

Formula of acid	Name of acid	Formula of salt	Name of salt
$HClO$	Hypochlor*ous* Acid	$KClO$	Potassium hypochlor*ite*
$HClO_2$	Chlor*ous* Acid	$KClO_2$	Potassium chlor*ite*
$HClO_3$	Chlor*ic* Acid	$KClO_3$	Potassium chlor*ate*
$HClO_4$	Perchlor*ic* Acid	$KClO_4$	Potassium perchlor*ate*

The only parts that are changed in the above list are those printed in italics. It is, accordingly, a very simple matter to name a salt, when the name of the corresponding acid is known.

88. Writing formulæ when the names of the substances are known.—If the valencies of all the elements and the names of the *-ic* acids are memorized, the formulæ of almost any substance used in elementary chemistry can be written.

In the following formulæ $P'''Cl'_3$, $Al'''_2O''_3$, $Na'_2(SO_4)''$, $Ca''_3(PO_4)'''_2$, the valency of the elements and radicles involved are indicated by accents placed above the symbols, Na' indicating that sodium is univalent, Ca'' that calcium is bivalent, etc. It will also be noticed, that in each of the formulæ the numbers indicating the valencies are inversely proportional to the number of the atomic weights of the elements or the number of the radicles; this rule is true generally. In phosphorus hydride, for example, the valency of phosphorus is 3, and the valency of hydrogen is 1, and the inverse ratio is 1 to

JOHN DALTON (1766-1844)

English chemist and natural philosopher. He was the son of a poor weaver. He spent twelve years as an assistant in a school at Kendal, during which time, through habits of observation and independent thought, he laid the foundation for future research. In 1793 he was appointed professor of mathematics and natural philosophy at New College, Manchester, and in 1822 was elected a Fellow of the Royal Society. He lived a life of simplicity and aloofness, working laboriously, often with crude apparatus, for the notable results he obtained. His name is closely linked with the atomic theory, which he was the first to enunciate. He discovered the phenomenon of colour blindness, experimented on the absorption of gases by water, on carbonic acid, and on carburetted hydrogen.

3; hence the formula is PH_3. Suppose, again, we wish to write the formula for aluminium carbide. We write first the two symbols together, and place the valency above each thus, $Al'''C''''$. Now, since the number of atomic weights is in the inverse ratio, the formula is Al_4C_3. Again, what is the formula of stannic sulphate? Tin in stannic compounds is quadrivalent, and the sulphate radicle is bivalent. We write the symbols first with the valencies above them thus, $Sn''''(SO_4)''$. The index numbers below will be in the inverse ratio to the valency numbers, hence they will be as 2 is to 4; the formula will, accordingly, be $Sn_2(SO_4)_4$, or more simply $Sn(SO_4)_2$. In a similar manner, with a knowledge of the valencies the formulæ of almost all the substances met with in elementary chemistry can be determined.

What, now, is the formula of calcium phosphite? Since the name of this salt ends in *-ite*, it is a salt of phosphorous acid. Phosphoric acid is H_3PO_4; phosphorous acid, is, therefore, H_3PO_3. Since the hydrogen is replaced in calcium phosphite by calcium, which is bivalent, the three atomic weights of hydrogen will be replaced by one and one-half atomic weights of calcium, thus, $Ca_{1\frac{1}{2}}PO_3$; which when multiplied through by 2 to clear it of fractions gives $Ca_3(PO_3)_2$.

89. Hydroxides.—The hydroxides may be considered derivatives of water which, when written HOH, can be called hydrogen hydroxide. The hydroxides are derived from water by replacing one of the atomic weights of hydrogen in each molecular weight by another element. Thus KOH is potassium hydroxide; NaOH is sodium hydroxide; and $Al(OH)_3$ is aluminium hydroxide. Accordingly, by replacing one atomic weight of hydrogen in each molecular weight of water by another element the formula of any hydroxide may be written.

QUESTIONS

1. $$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2.$$
What weight of zinc can be dissolved in 10 grams of sulphuric acid? How much zinc sulphate will be formed? What weight of hydrogen is produced and what volume does it occupy at N.T.P.?

2. How many litres of hydrogen measured at N.T.P. can be obtained when 8 grams of iron are acted on by sulphuric acid?

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2.$$

3. The following weighings were made when crystals of barium chloride were heated in a crucible: Weight of empty crucible 40.7447 grams; weight of crucible + crystals before heating 43.7567 grams; weight of crucible + white powder after heating 43.3130 grams. If the equation representing the reaction is $BaCl_2 . xH_2O \longrightarrow BaCl_2 + xH_2O$, find the value of x.

4. If 0.109 grams of cadmium release from an acid 24.4 c.c. of hydrogen at 20° C. and 740 mm. pressure and the atomic weight of cadmium is 112.4, what is the valency of cadmium?

5. If 0.203 grams of magnesium liberate 195.5 c.c. of hydrogen at 13° C. and 760 mm., and if 0.509 grams of zinc liberate 183 c.c. at 9° C. and 748 mm. pressure, find the valencies of these two elements ($Mg = 24.4$, $Zn = 65.4$).

6. Explain how the weight of hydrogen displaced by a known weight of metal may be found without actually weighing the hydrogen.

7. Write names for the substances represented by the following formulæ: KCl, Na_2O, NH_3, P_2O_3, P_2O_5, CuS, $CuBr_2$, $CuBr$, H_2O.

8. Write formulæ for the following substances: sodium chloride, calcium bromide, aluminium oxide, mercuric iodide, mercurous iodide, silver sulphide, magnesium nitride (nitrogen is trivalent), antimonious chloride, antimonic chloride.

9. Write names for the substances represented by the following formulæ: K_2SO_4, $NaClO$, H_3PO_2, $Zn(OH)_2$, $AlPO_4$, $MgSO_3$, $Ca(ClO_3)_2$, Na_2CO_3, $Sn(OH)_4$, $HClO$, $Ca(ClO_4)_2$.

10. Write formulæ for the following substances: magnesium sulphate, calcium nitrate, sodium hypochlorite, calcium hypophosphite, potassium perchlorate, calcium hydroxide, nitrous acid.

CHAPTER X

THE ATOMIC AND MOLECULAR THEORIES

90. Hypothesis and theory.—

> "One-story intellects, two-story intellects, three-story intellects with skylights. All fact-collectors, who have no aim beyond their facts, are one-story men. Two-story men compare, reason, generalize, using the labours of the fact-collectors as well as their own. Three-story men idealize, imagine, predict; their best illumination comes from above, through the skylight."
>
> —*Oliver Wendell Holmes*

We have stated some of the quantitative principles of chemistry—the law of the conservation of mass, the law of the conservation of the elements, the law of definite proportions, the law of multiple proportions, Gay-Lussac's law of volumes, and finally the remarkable law of combining weights. The questions naturally rise in everybody's mind: What is the explanation of all these laws? What is the cause of this remarkable behaviour of matter when it undergoes chemical change? When the facts have been discovered and such questions arise, the scientist endeavours to construct by means of the imagination a picture representing matter at work, and to see if, from his imaginary picture, he can deduce the facts.

An assumed explanation of facts is called an *hypothesis;* and if by the hypothesis one is able, as time passes, to explain and unify many of the facts, it becomes a *theory.* The two terms, however, are used somewhat loosely by scientists.

91. The Atomic theory.—

> "The hypothesis known as Dalton's atomic theory may be said to have become one of the most important foundation stones of the science, and to have exerted an influence on its progress greater than that of any other generalization, with, perhaps, the single exception of Lavoisier's explanation of the phenomena of combustion and the discovery of the indestructibility of matter." —*Sir Henry Enfield Roscoe*

In 1803-4, John Dalton, the famous discoverer of the laws of definite and of multiple proportions, formulated the atomic theory, which offered a simple explanation of the fundamental chemical laws. Instead of giving his picture of matter at work, the theory will be more easily understood if we present it as it stands to-day; for some additions and modifications of the theory, as enunciated by Dalton, have since been necessary, in order to bring it into harmony with all the known facts. All pure substances are pictured as being made of little particles called *molecules.* The molecules of each substance are of the same weight, but the molecules of different substances differ in weight. Thus the molecules of hydrogen are all of exactly the same kind and weight, but are different in kind and weight from the molecules of water, which again are all of the same kind and weight. These molecules are the smallest existing particles of any substance. If the molecule is divided, the pure substance disappears and other pure substances are formed. Again, each molecule of an element is composed of still smaller particles called *atoms.* These atoms in the molecule of an element are all of the same kind and weight; but the atoms of the different elements are of different kinds and weights. There are thus about eighty different kinds of atoms, corresponding to the number of the different elements. The molecules of compound substances are composed of these same elementary atoms; but the atoms in the molecule of a compound are always of two or more kinds, corresponding to the number of its elementary constituents. These atoms, even in an element, do not usually exist alone, but generally several are combined to form a molecule. As all the molecules of a substance have the same weight, they are each considered to be composed of exactly the same number and of the same kinds of atoms. The number of atoms in a molecule is usually quite small; thus the molecule of oxygen is composed of two atoms of oxygen; that of water of one atom of oxygen and two atoms of hydrogen. As the atoms pass from molecule to molecule in a chemical reaction, they always retain the same weight.

Dalton was not the originator of the idea that the atoms are not in immediate contact, but that there are spaces between them. Some of the Greek scholars, who lived in the very infancy of civilization, had put forth this doctrine. The idea was revived in modern times, and both Sir Isaac Newton and Sir Robert Boyle accepted the theory of atoms. Dalton, however, by giving it a quantitative significance, made it so powerful in the hands of chemists that, as the quotation at the beginning of the section indicates, more of the discoveries of modern chemistry are attributable to it than to any other cause.

92. Its explanation of the chemical laws.—

> "We have not yet any theory sufficiently developed which can explain all the facts of chemistry as simply and as consistently as the atomic theory developed in modern chemistry."
>
> —*H. L. F. Helmholtz*

When two substances react to form other substances, they merely exchange their atoms; there is no loss in the number of atoms, but merely a change in their distribution. There will be, therefore, no change in total weight, as stated in the law of the *conservation of weight.* Again, when the atoms of the elements pass from one substance into another, there can be no permanent loss of any part of an element, as there is merely an exchange among the substances, and the atoms that unite to form a substance can always be obtained from that substance again. This explains why the elements are conserved as stated in the law of the *conservation of the elements.*

When atoms of different elements combine to form a molecule of a substance, they usually unite in small numbers. In mercury oxide, one atom of mercury unites with one atom of oxygen. Now as every atom of an element has the same weight, the proportion of oxygen to mercury in mercury oxide must always be the same as the relative weights of their atoms. The pure substance, water, is composed of molecules, each of which contains two atoms of hydrogen and one atom of oxygen. The proportions of these two elements in water will, therefore, always be constant; and a large number of experiments have justified chemists in concluding that what is true of these two substances is equally true of all substances. Thus the atomic theory explains the *law of definite proportions.*

Carbon monoxide and carbon dioxide are both composed of the same elements, carbon and oxygen. The molecule of the former contains one atom of carbon and one atom of oxygen; while that of the latter contains one atom of carbon and two atoms of oxygen: that is, the amounts of oxygen combined with one atom of carbon in the two substances are as one to two, or simple multiples of each other. In all sets of substances, each of which contains the same elements, a like arrangement obtains. For, if we consider the simplest molecule of a compound, which is a member of a set, to be composed of one or two atoms of each of its constituents, then the other molecules of the set must be formed by adding one, two, or some other small number of atoms to this simplest molecule. For example, nitrogen and oxygen form five oxides, whose molecules have the composition shown in the following table:

Name	No. of nitrogen atoms	No. of oxygen atoms	Ratio of No. of atoms
Nitrous oxide...........	2	1	2:1
Nitric oxide............	1	1	2:2
Nitrogen trioxide.......	2	3	2:3
Nitrogen peroxide.......	1	2	2:4
Nitrogen pentoxide......	2	5	2:5

The last column in this table shows that the numbers of atoms of oxygen that unite with a fixed number of atoms of nitrogen—two in this case—bear a simple ratio to one another, namely, 1:2:3:4:5. As these atoms of nitrogen are all of equal weight, the amounts of oxygen that unite with a fixed quantity of nitrogen are simple multiples of one another. The same is true of all such sets of compounds. This is *the law of multiple proportion.*

Substances react molecule with molecule, or two molecules of one with one molecule of the other, or in some such simple proportion. If we were to set down the weights of the molecules of all substances, the substances react in the proportion of these weights when they react molecule with molecule; or in the proportion of simple multiples of these weights when several molecules of one substance react with one or more molecules of another. This is *the law of combining weights*, and it is evident how admirably it is explained by the molecular theory.

93. Avogadro's hypothesis and Gay-Lussac's law of volumes.—

> "Avogadro's hypothesis has proved to be one of the most suggestive and fruitful hypotheses in the development of chemistry. It has correlated what appeared antagonistic and contradictory, it has harmonized what seemed discordant and confused, and has made Dalton's atomic hypothesis a clear, intelligent, and fertile theory."
>
> —*Charles Adolphe Wurts, 1878*

In Section 55 we saw that, according to Avogadro's hypothesis, equal volumes of all gases, at the same temperature and pressure, contain equal numbers of molecules. And in Section 92 we saw, also, that when two substances react, they react molecule with molecule, or the number of molecules that react is always small. Accordingly, if they react molecule with molecule, they must react in equal volumes. If, also, one molecule of one reacts with two molecules of another, one litre of one reacts with two litres of the other, as a litre of each gas contains the same number of molecules. Hence gases react in equal volumes, or in volumes having a simple proportion, and this is Gay-Lussac's *law of combining volumes.*

We have thus started with the imaginary picture of the working of matter as presented by the atomic and molecular theories, and have found that all of the great quantitative laws of chemistry can be deduced therefrom. Experiment also proves that the deduced laws are in accordance with facts, and this is the great test of an hypothesis. No better example can be given of the value of a theory thus treated than that of the atomic theory; for many of the great facts of chemistry which have been discovered since this theory was enunciated, have been first deduced from this theory, and only afterwards proved experimentally.

94. Molecular weights and atomic weights.—It is quite impossible to weigh a molecule, for it is so small that it would fail to turn the most delicate balance, even if we were able to isolate a single one in order to place it on the pan. But while we cannot weigh a single molecule, it is possible to find the relative weights of different molecules. According to Avogadro's hypothesis a litre of hydrogen, a litre of oxygen, and a litre of carbon dioxide all contain equal numbers of molecules. If we weigh a litre of each, the weights thus obtained will bear the same proportion to one another as the weights of the single molecules. It is not, however, necessary to weigh a litre of each, for any equal volumes will give the relative weights of the molecules. Earlier in this volume the weights of 22.4 litres of all gases at N.T.P. have been called the molecular weights; for example:

22.4 litres of oxygen at N.T.P. weigh 32 grams
22.4 " " hydrogen " " 2 grams
22.4 " " carbon dioxide " " 44 grams
22.4 " " ammonia " " 17 grams.

These are the results obtained by weighing equal volumes—22.4 litres—of each gas. The relative weights of the molecules are therefore 32, 2, 44, 17. These numbers, expressed in grams, we have called the molecular weights, but these numbers also express the relative weights of the molecules, and that is the reason they were primarily called molecular weights.

We have now given two meanings to the term molecular weight. Theoretically it means the relative weight of the molecule to that of oxygen which is taken as 32; and experimentally it means the weight of 22.4 litres of a gas N.T.P. The latter, which we have called the molecular weight, is frequently called the *gram molecular* *weight* or *molar weight*, the former being used for the relative weights of the molecules. We will, however, continue to use the term, gram molecular weight, to signify the weight of 22.4 litres of the gas at N.T.P., and also the relative weights of the molecules when compared with that of oxygen taken as 32.

The smallest weight of an element which occurs in a gram molecular weight of a substance has been called its atomic weight. The smallest amount of an element which occurs in any molecule of a substance is an atom. These same numbers, then, which we have called atomic weights, express the relative weights of the atoms Thus the term atomic weight also has a theoretical as well as an experimental significance. Hence the symbol of an element can be considered to stand for an atom of the element. In studying formulæ and equations the pupil should never forget the double significance of the symbols and formulæ, and should be prepared to interpret them either in terms of the atomic theory or in terms of their quantitative experimental value.

Many other phenomena admit of explanation in terms of the atomic theory, and such explanation will be given when the phenomena are being described.

95. Recent discoveries regarding the structure of matter.—The law of the conservation of the elements had long seemed to be one of the best established laws of chemistry (Sec. 33). The early alchemists did not recognize its validity and were ceaselessly endeavouring, always without success, to find a way by which the baser metals, such as lead, could be converted into silver and gold. Within recent years, however, some most remarkable substances have been discovered; and a careful study of them has weakened our belief in the law of the conservation of the elements. Indeed, the dream of the alchemists

SIR WILLIAM RAMSAY (1852-1916)

Scottish chemist, born at Glasgow. He held the chair of chemistry in University College, London. In earlier life he was interested chiefly in organic chemistry, but later he devoted his talents to the investigation of the problems of inorganic and physical chemistry. As an experimenter, he worked with extreme rapidity and yet with the greatest skill and accuracy. He was able by means of the microbalance to weigh volumes of gas much smaller than the head of a pin. In conjunction with Lord Rayleigh he discovered several new elements in the atmosphere, which he named argon, neon, krypton, and xenon. He also discovered helium, and apparently realized the dream of the alchemists by converting one metal into another, for from radium he obtained helium, and from copper, lithium.

seems about to be realized, but in a way of which they did not dream. One of the most remarkable of these new substances is radium. It is difficult to procure, is many times as valuable as gold, and has remarkable electrical properties. It has all the characteristics of an element; its atomic weight is known, its valency, its physical and chemical properties, and its salts have been studied. Yet it continually gives off a gas called *niton*, which also is considered an element. This action is not an ordinary chemical change; for it is not affected by heat or concentration, nor can the rate of reaction be increased nor decreased. And not only niton but also *helium* is a product of the disintegration of radium, and there is some ground for believing that lead is also a product of the disintegration of the same substance.

Sir William Ramsay has contributed an important experiment which affords additional grounds for belief in the transmutation of the elements. He sealed copper nitrate in a glass tube with niton, and in time the metal lithium was detected in the tube, though the greatest precautions had been taken to see that no lithium was allowed to enter. Some chemists now believe that, under the influence of the niton, the copper was transmuted into lithium. And other careful experiments give some ground for believing that carbon can be produced from lead, and that hydrogen can be built up into *neon* and helium, two of the rarer elements.

Thus it appears that there are some reasons for believing that the atom itself is capable of being decomposed. We may, therefore, look forward to a new era in the study of science, when a new kind of change, perhaps neither physical nor chemical, will allow one element to be transmuted into another.

QUESTIONS

1. State the chief terms of Dalton's atomic theory, and of the molecular theory.

2. State the facts which the atomic theory attempts to explain.

3. HCl is the formula for hydrogen chloride. State the theoretical and experimental significance of the formula. Which is more useful in solving quantitative problems?

4. The formula for oxygen is O_2, for ozone O_3. Both are gases. Suggest how these formulæ can be experimentally obtained. Give an explanation of the change of oxygen into ozone, in terms of the atomic theory.

5. $2\,O_3 \rightarrow 3\,O_2$ is the equation representing the conversion of ozone into oxygen. When one litre of ozone is converted into oxygen, what volume of oxygen is produced? Explain this in terms of Avogadro's hypothesis.

6. Explain in terms of the atomic and molecular theories what happens when potassium chlorate is heated.

7. Deduce the law of combining weights from the atomic theory.

8. Explain the difference between univalent, bivalent, trivalent, etc., elements, in terms of the atomic theory.

9. What is the difference between an atom and a molecule? Is it correct to speak of an atom of hydrogen, an atom of water, a molecule of oxygen, an atom of sulphur, a molecule of air, an atom of mercury oxide, a molecule of brine?

CHAPTER XI

COMMON SALT AND ITS PRODUCTS

COMMON SALT

96. Occurrence.—Common salt is by far the most abundant of all the soluble salts. It is found in the greatest quantities in the oceans, where every gallon of water contains one quarter of a pound of salt. Besides this, salt is found in great beds in the crust of the earth, which are undoubtedly composed of the salts deposited from seas now dried up. One of these salt beds was laid down millions of years ago in Western Ontario and the adjoining part of Michigan, and when the superimposed rocks are drilled through, the salt beds are penetrated. At Goderich, Sarnia, Windsor, and neighbouring towns, much salt is mined in this way.

97. Physical properties.—When a single grain of common salt is examined, it is found to have the form of a little cube more or less perfect. It is quite transparent, but when the crystals are seen in mass the salt appears white. Its taste is well known. It dissolves in water, the solution being called brine. Its solubility is about the same in hot and cold water, as can be learned from a study of Figure 26, 100 c.c. of water dissolving about 37 grams of the salt. When heated intensely it melts without any chemical change. Ordinary salt also becomes damp in humid weather, for magnesium chloride, an impurity in it, is deliquescent.

98. Chemical properties.—When common salt reacts with sulphuric or phosphoric acid, a suffocating gas is produced called hydrogen chloride:

$$H_2SO_4+NaCl \rightarrow NaHSO_4+HCl.$$

If silver nitrate is added to brine, a white precipitate of silver chloride is produced, and this precipitate is soluble in ammonia, but insoluble in nitric acid. If a solution of common salt is placed in an evaporating dish, and a colourless flame is brought down on its surface, the reflected flame is coloured intensely yellow. These last two chemical properties are distinguishing tests of common salt, but usually its taste alone will distinguish it from every other substance.

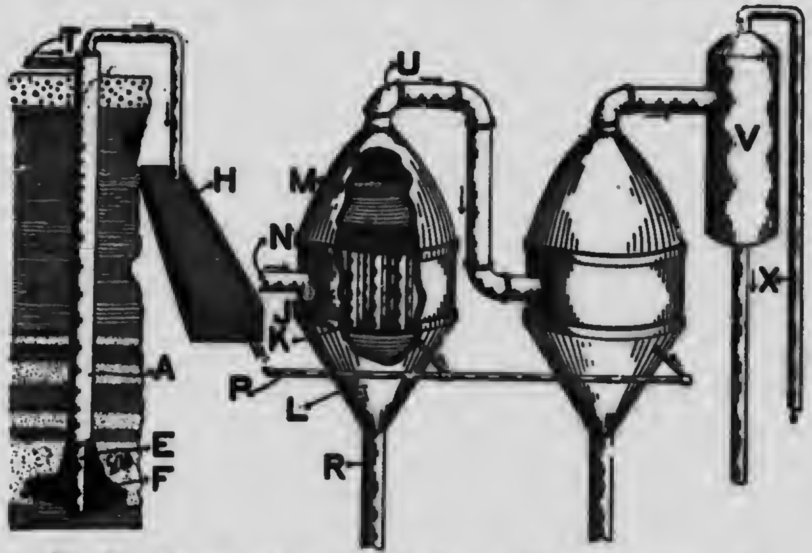


FIG. 31.—SECTION THROUGH SALT WELL AT LEFT. EQUIPMENT FOR EVAPORATING THE BRINE AT THE RIGHT

The coarsely stippled layer represents drift; the finely stippled layers, salt beds; and the wavy-lined layers, limestone. A. Casing through which water is forced down. E. Inner pipe through which the brine is pumped up. F. Cavity in salt bed containing brine. H. Settling tank. J. Steam chest with vertical tubes (K) running from the evaporating dome above (M), to the bottom cone (L). N. Tube bringing steam to steam chest. P. Pipe by which brine is led from the settling tank (H) to the evaporators. R. Tube through which deposited salt is removed. U. Pipe carrying the steam from one evaporator to the next in the series. V. Condenser. X. Pipe leading to air-pump.

99. Commercial importance. — Common salt is called rock-salt by miners, halite by mineralogists, sodium chloride by chemists, and ordinarily just "salt". Large quantities of it are used for preserving meats and as food for man and beast, and in the manufacture of other chemicals, such as washing-soda, baking-soda, and bleaching-powder. It is also much used as a fertilizer. In warm countries the sun's rays are used to prepare it by evaporation from sea-water. In Germany and Austria it is mined by sinking a shaft to the salt beds. In Canada and the United States a hole about eight inches in diameter is drilled to the salt bed, and water is run into the hole. When it has dissolved the salt, it is pumped up and evaporated in shallow pans heated by furnaces. As the salt is deposited in the pans it is raked out and allowed to drain. A process more perfect than this is being introduced and is now in operation at Windsor, where the largest salt-producing plant in Canada is located. The water is forced down an outer tube (Fig. 31, A), and the brine is forced up an inner tube (E) into a settling tank (H). It is then passed into a succession of cylindrical tanks, where it is warmed by steam entering at (N). The space in the tank above the brine is kept exhausted by an air-pump, and thus evaporation takes place very rapidly. The salt is precipitated and collected through the pipe (R). Nearly half a million dollars' worth of salt is produced in Ontario every year.

HYDROGEN CHLORIDE

100. History.—Glauber prepared this gas in 1648, much as it is prepared at the present day, but he did not know how to collect it. This was accomplished by Priestley, who discovered the method of collecting gases over mercury.

For a time a controversy raged over the composition of this gas. Lavoisier and his fellow French chemists believed that it contained oxygen; but Sir Humphrey Davy finally settled the dispute in 1810 by proving conclusively by experiment that it contains only hydrogen and chlorine.

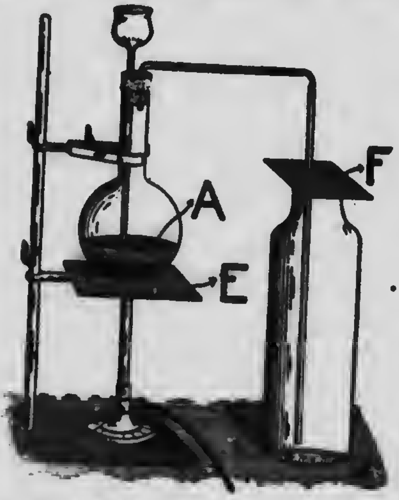


FIG. 32.—APPARATUS FOR PREPARATION OF HYDROGEN CHLORIDE

A. Sodium chloride and sulphuric acid. E. Asbestos sheet. F. Cardboard, covering bottle in which gas is collected.

101. Preparation. — In the laboratory it is usually prepared through the action of strong sulphuric acid on common salt. The salt is placed in a flask (Fig. 32), and sulphuric acid is added through a thistle-tube. As the gas is heavy and very soluble, it is best collected by displacement of the air, as represented in the Figure. The usual reaction is expressed by the following equation:

$$H_2SO_4+NaCl \rightarrow NaHSO_4+HCl.$$

But if the mixture is intensely heated, a further reaction takes place:

$$NaHSO_4+NaCl \rightarrow Na_2SO_4+HCl.$$

Any other metallic chloride could be used, but as sodium chloride is much the cheapest, the gas is always prepared in the laboratory and commercially from the two substances just mentioned.

102. Properties.—Hydrogen chloride is composed of chlorine and hydrogen in the proportion of 35.5 to 1, and 22.4 litres of it at N.T.P. weigh 36.5 grams; therefore its formula is HCl. It has a very irritating smell and injures the throat and lungs if inhaled. When it comes in contact with moist air the moisture is condensed into a cloud. It dissolves with avidity in water, 1 c.c. of water at 0°C. dissolving more than 500 c.c. of the gas. If a dilute solution of the gas is boiled, it gives off a mixture containing a larger proportion of water than the solution contains; and if a concentrated solution is boiled, it gives off a mixture containing a smaller proportion of water than the solution contains. If the boiling of both the dilute and the concentrated solution is continued, the former will become more concentrated and the latter more dilute, until they finally reach the same composition, each having 20 per cent. of hydrogen chloride. If the boiling of either is continued still further, the liquid remains unchanged in composition, the hydrogen chloride and water being driven off in the proportions in which they are present in the liquid. It is thus impossible to separate the hydrogen chloride and water by boiling.

The dry gas does not act on litmus, marble, or zinc. If, however, it is passed over sodium in a combustion tube, as in Figure 33, it reacts readily with the sodium. The sodium is placed in the bulb (H), and the hydrogen chloride generated in the usual way. The gas is passed through a U-tube containing lumps of pumice-stone (F), soaked in sulphuric acid in order to dry it, and it is then passed over the sodium. When the air has all been expelled from the apparatus, the sodium is ignited; as soon as it begins to burn a blazing splint is put to the jet attached to the end of the combustion tube, and the escaping hydrogen ignites. If preferred, the hydrogen may be collected over water. This experiment proves that the hydrogen chloride contains hydrogen. If the substance in the bulb is tasted, it is found to be sodium chloride. The following equation represents the reaction:

$$2Na+2HCl \rightarrow 2NaCl+H_2.$$

Potassium and magnesium also burn in hydrogen chloride with the liberation of hydrogen. If the gas mixed with oxygen is passed through a combustion tube containing lumps of pumice-stone soaked with a solution of copper chloride, a coloured gas issues from the tube, which must have come from the hydrogen chloride, as the copper chloride is unchanged. This gas is *chlorine.* The oxygen unites with the hydrogen of the gas. The equation representing the reaction is as follows:

$$4HCl+O_2 \rightarrow 2H_2O+2Cl_2.$$

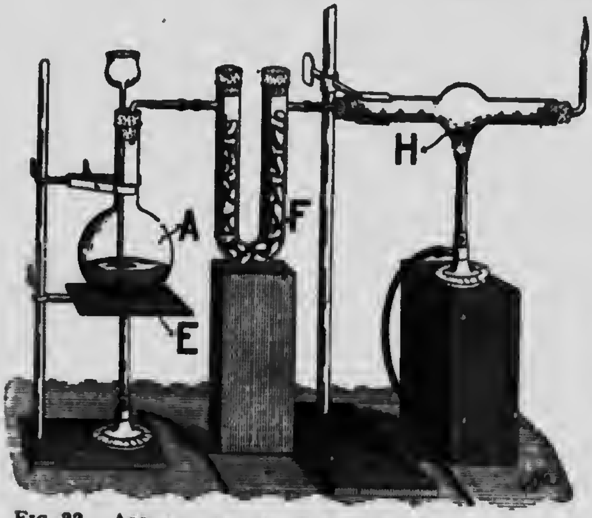


FIG. 33.—APPARATUS TO SHOW THAT HYDROGEN CHLORIDE CONTAINS HYDROGEN AND CHLORINE

A. Hydrogen chloride generator. E. Asbestos sheet. F. U-tube containing pumice-stone soaked with sulphuric acid. H. Bulb-tube containing sodium.

Thus it can be proved that hydrogen chloride contains both hydrogen and chlorine.

103. Properties of hydrochloric acid.—A solution of hydrogen chloride in water is called hydrochloric acid, and sometimes muriatic acid. It turns blue litmus red and acts on zinc, liberating hydrogen; it also acts quite readily on magnesium, iron, and aluminium:

$$Zn+2HCl \rightarrow ZnCl_2+H_2.$$

In each case it forms the chloride of the metal. It also acts on marble or other carbonates, liberating carbon dioxide and forming the chlorides of the metals. An alcoholic solution of the gas is also an acid, having properties similar to those just mentioned, but when it is dissolved in benzine, kerosene, or toluene, it acts quite differently, for the solution has no effect on litmus, zinc, or marble.

104. Commercial importance.—Large quantities of this acid are prepared as a by-product in the manufacture of soda. At first in the manufacture of soda this gas was allowed to escape into the air, but it is so destructive to vegetation that the whole neighbourhood for miles around was turned into a desert. Manufacturers were then compelled by law to collect the gas, though it was a useless product. Soon, however, it was discovered that bleaching-powder could be made from it, and that, accordingly, it is a very valuable by-product, and manufacturers, who considered themselves badly treated when they were compelled to collect the gas, soon recognized that it had become one of their chief sources of profit. Its method of preparation will be more fully described when the manufacture of soda is being discussed.

CHLORINE

> "I took a retort containing a mixture of manganese (manganese dioxide) and *acidum salis* (acid made from salt). In front of the neck I bound a bladder emptied of air and set the retort on hot sand. The bladder became distended by the effervescence in the retort . . . . I removed the bladder and found that this air (gas) had coloured it yellow . . . It had, however, a quite characteristically suffocating smell, which was most oppressive to the lungs."
>
> —*Karl Wilhelm Scheele, 1774*

105. Historical.—This remarkable gas was first prepared by the great Swedish chemist Scheele, in 1774. In the quotation at the head of this section is given in his own words the first description of its preparation, and Figure 34 shows his drawing of the apparatus he used. He called the gas dephlogisticated marine acid air, air being a name given to all gases, and marine acid being another name for hydrochloric acid. For a long time chlorine was supposed to be composed of hydrogen chloride and oxygen, and hence was called oxymuriatic gas. But in 1810 Sir Humphry Davy, after subjecting it to all sorts of severe chemical tests in an endeavour to extract oxygen from it, finally proved that it contained none, and that it was an element. As the old name, oxymuriatic gas, was misleading, he gave it, on account of its colour, its modern name chlorine, which is derived from a Greek word meaning pale green.

FIG. 34.—SCHEELE'S ORIGINAL DRAWING OF HIS METHOD OF PREPARING CHLORINE AND COLLECTING IT IN A BLADDER

The retort was heated in a charcoal furnace.

106. Occurrence.—Chlorine, as we shall soon find, is a very active element, readily uniting with many substances; hence it is not found in the free state, but always combined with other elements. Its chief source is the chlorides of sodium, potassium, and magnesium, which are found in sea-water and in great salt beds, as has been already stated in describing common salt. Sodium chloride, which is by far the most abundant of these salts, is the source of all the chlorine that is used commercially.

KARL WILHELM SCHEELE (1742-1786)

Swedish chemist. He was apprenticed at fourteen to an apothecary in Gothenburg. Later he was proprietor of a pharmacy at Köping. Despite a life of constant hardship, the record of his discoveries is unparalleled. Most of his work was accomplished at the end of busy days, in narrow chambers, with apparatus of his own inventing; but the spirit within him was unquenchable. He stands unique among experimental investigators, his dexterity in manipulation being unsurpassed. Among his contributions to Science are his independent discovery of a great number of important acids, such as tartaric, benzoic, lactic, citric, and oxalic; and his preparation of chlorine, baryta, oxygen, glycerine, and sulphuretted hydrogen. He also showed the chief components of the atmosphere to be two gases, one supporting combustion and the other destroying it.

107. Laboratory preparation.—Chlorine is usually prepared from hydrochloric acid, which, as we have learned already, is composed of hydrogen and chlorine. In order to liberate the latter, it is necessary to add some substance that will unite readily with the hydrogen and thus set free the chlorine. Of such substances we naturally select oxygen, as it unites vigorously with hydrogen and produces great heat. If oxygen and hydrogen chloride are passed through a red-hot tube, a certain amount of chlorine is formed, but it is small in quantity and mixed with large quantities of the unchanged gases:

$$4HCl+O_2 \rightarrow 2H_2O+2Cl_2.$$

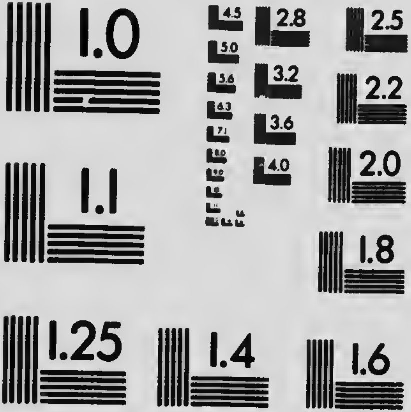
In practice it is found more satisfactory to use, rather than the oxygen itself, a compound that readily liberates oxygen. Accordingly, any of the substances which we found (Sec. 11) to give off oxygen when they are heated, such as potassium chlorate, red lead, manganese dioxide, or saltpetre, will serve. When they are mixed with hydrochloric acid and heated, chlorine is produced in every case, but some of them produce other gases as well, so that both commercially and in laboratory work manganese dioxide is generally used. The solid is put in a flask (Fig. 32), hydrochloric acid is poured through a thistle-tube, and the flask is gently heated. The gas produced, as it is quite heavy, is readily collected by displacing air. It can also be collected over warm water, or better still over a warm salt solution; but not over cold water, as it is quite soluble in the latter. The reaction is expressed by the equation:

$$MnO_2+4HCl \rightarrow MnCl_2+Cl_2+2H_2O.$$

Many other methods of preparing chlorine may be used, but only one other will be mentioned, because it is an excellent one for the laboratory. In this method, chloride of lime is used instead of manganese dioxide,

MICROCOPY RESOLUTION TEST CHART

(ANSI and ISO TEST CHART No. 2)



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and hydrochloric acid is added to it. The reaction will be better understood after chloride of lime has been studied.

108. Physical properties.—Chlorine, the first coloured gas that we have studied, is greenish-yellow and has a very disagreeable, irritating odour. It is a heavy gas, as 22.4 litres of it at N.T.P. weigh 71 grams; and since the symbol Cl stands for 35.5 grams, the formula is Cl_2. If inhaled it produces serious effects and may cause death. On account of its poisonous character pupils should be careful not to allow it to escape into the laboratory. If it should be inhaled, some relief can be obtained by inhaling the vapour of alcohol. This is the gas that the German army used with such deadly effect against the Canadians at the Battle of St. Julien. A litre of cold water dissolves four litres of the gas to form a yellowish-green liquid, called chlorine water; this liquid smells and tastes like the gas. If chlorine is passed into ice-cold water, yellow crystals of a substance called chlorine hydrate, $Cl_2.8H_2O$, are formed. Chlorine can be readily converted into a liquid and into a solid. The conversion of the gas into a liquid was accomplished by Faraday in an interesting manner. During very cold weather he prepared crystals of chlorine hydrate, dried them, and placed them in a glass tube, which was then sealed. A friend of his, examining his tube, noticed a yellow oily liquid on the inside and rallied Faraday for using greasy tubes. As Faraday was filing the tube open to obtain the yellow oil, the contents exploded and shot out violently. He wrote to his friend the next morning that the experiment had been repeated, and that the oily liquid was nothing less than liquid chlorine. He was able to liquefy it in larger quantities by using an inverted V-shaped tube (Fig. 35), in one arm of

MICHAEL FARADAY (1791-1867)

English chemist and physicist. He was the son of a poor blacksmith, who apprenticed him at an early age to a London bookbinder. During his leisure time he occupied himself in the construction of an electrical machine and other apparatus. Sir Humphry Davy became interested in the lad, and, in 1813, procured him a position as laboratory assistant in the Royal Institution, of which he was later appointed professor of chemistry. As a scientist, he was keen, persistent, far-seeing, and tireless, accurate in experiments, and convincing in the results he obtained. He discovered methods of liquefying gases, and also discovered new compounds of chlorine and carbon, and of hydrogen and carbon. He investigated the decomposition of alloys of steel; and he prepared new kinds of glass. His greatest discoveries, however, were in the field of electricity.

which chlorine hydrate crystals were placed. The tube was then sealed, and the empty arm surrounded by a freezing mixture. When the other arm was heated, the chlorine was driven off from the hydrate and produced such a great pressure that it was liquefied in the arm surrounded by the freezing mixture. By this principle Faraday also liquefied many other gases.

109. Chemical properties.—As chlorine is an exceedingly active element, it combines directly with nearly all of the other elements, nitrogen, oxygen, and carbon being the three chief exceptions. If copper or iron in the form of a thin wire is first heated and then inserted into a bottle of the gas, combustion follows with the formation of copious fumes of the chlorides:

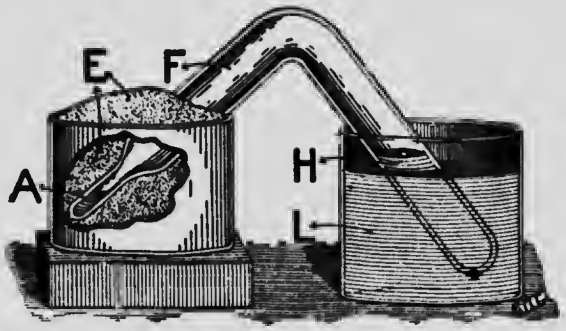


FIG. 35.—FARADAY'S METHOD OF LIQUEFYING CHLORINE A. Liquid chlorine. E. Freezing mixture. F. Glass tube. H. Chlorine hydrate. L. Warm water.

$$Cu+Cl_2 \rightarrow CuCl_2,$$
$$2Fe+3Cl_2 \rightarrow Fe_2Cl_3.$$

Powdered antimony does not require to be heated, but ignites spontaneously when sprinkled in the gas, producing dense fumes and flashes of light. Magnesium powder, without any flash of light, is converted into white magnesium chloride. A piece of sodium dropped into the gas gradually becomes covered with a white coating, which, on examination, turns out to be common salt or sodium chloride:

$$2Na+Cl_2 \rightarrow 2NaCl.$$

This latter reaction reveals in a striking manner the mystery of chemical change. By combining a yellow, irritating, poisonous gas with a soft metal that the slightest contact with water would set on fire, we obtain a valuable food material which is neither irritating, poisonous, nor inflammable, but so palatable and necessary for food that people and even wild animals will travel many miles in order to satisfy the natural craving for it. Chlorine unites just as vigorously with some of the non-metals, for phosphorus ignites spontaneously in it to form one of the chlorides,

$$2P+5Cl_2 \longrightarrow 2PCl_5, \text{ or}$$
$$2P+3Cl_2 \longrightarrow 2PCl_3,$$

according to the relative quantities of the two elements present. Its most important chemical property, however, is the intensity with which it reacts with hydrogen. When mixed, the two gases unite with explosive violence if exposed to direct sunlight, and form hydrogen chloride; while, if the mixture is left in diffused sunlight, the gradual disappearance of the colour indicates the combination of the two to form the same substance:

$$H_2+Cl_2 \longrightarrow 2HCl.$$

In darkness, however, the mixture may be kept for years without the two combining. Not only does chlorine combine explosively with hydrogen, but it withdraws the hydrogen from many of the compounds of the latter. Paraffin, for example, is composed of compounds containing carbon and hydrogen. If a lighted paraffin candle is lowered into a bottle of chlorine it continues to burn, but with a very smoky flame, for the hydrogen of the paraffin combines with the chlorine, and the carbon is deposited as soot. The same phenomenon is exhibited by turpentine, $C_{12}H_{16}$, for if a filter paper is dipped into the warmed liquid and lowered into a bottle of chlorine, the turpentine bursts into a flame, and the carbon of the turpentine produces a dense cloud of smoke:

$$C_{12}H_{16}+8Cl_2 \longrightarrow 12C+16HCl.$$

110. Properties of chlorine water.—Many of the foregoing reactions will not take place if both reagents are perfectly free from water vapour. Perfectly dry chlorine and hydrogen, even in bright sunlight, undergo no combination. Again, neither copper, iron, nor sodium will combine with chlorine, except in the presence of a trace of water. Water in these circumstances probably acts as a catalyst.

If chlorine water is exposed to the sunlight, there arise bubbles of a gas, which can be proved to be oxygen. The disappearance of the greenish-yellow colour indicates the destruction of the chlorine; while the liquid which remains is hydrochloric acid. When chlorine combines with the hydrogen of water the oxygen is available for oxidizing. Hence we say that wet chlorine is an oxidizing agent. This latter property is well shown by boiling litharge, PbO, or red lead, Pb_3O_4, with chlorine water, when the suspended powder turns from yellow or red to dark brown; and on filtering the mixture, the brown residue, lead peroxide, PbO_2, is left on the paper. If this brown powder is heated strongly, it again gives off the oxygen which it had withdrawn from the water.

111. Bleaching with chlorine.—This oxidizing power of moist chlorine makes it useful for bleaching and disinfecting. When dyes and other coloured substances, such as ink, which contain hydrogen and carbon, are placed in contact with moist chlorine, the chlorine combines with the hydrogen of the water, and the oxygen of the water combines with the hydrogen and carbon of the coloured substances, thus oxidizing the latter to colourless compounds. Thus we see that the chlorine does not unite directly with the coloured substances, and hence is unable to bleach when it is perfectly dry. As chlorine does not re-act with carbon it has no bleaching effect on printing ink, which is composed largely of lamp black; nor on lead-pencil marks, which are composed of graphite, an allotropic form of carbon.

112. Resisting gas attacks in war.—It is interesting to examine the method used to overcome the gas attacks of the Germans in the Great War. The respirators, placed over the mouth and nostrils of the soldiers, were wetted with a strong solution of sodium thiosulphate, $Na_2S_2O_3$. The action of the respirators affords another example of the oxidizing power of chlorine in the presence of water. Sodium thiosulphate is a substance that has a marked tendency to deposit sulphur and to take up in its place oxygen from oxidizing agents, thus:

$$Na_2S_2O_3+O \longrightarrow Na_2SO_4+S,$$

the product being sodium sulphate. The whole reaction might be represented by the equation:

$$Na_2S_2O_3+H_2O+Cl_2 \longrightarrow 2HCl+Na_2SO_4+S.$$

Thus the chlorine, as soon as it comes into contact with the respirator, is converted into hydrogen chloride, which dissolves in the water. The air, thus freed from its poisonous gases, passes through.

113. Test for hydrochloric acid and chlorides.—If hydrochloric acid, or a solution of any metallic chloride, has a silver nitrate solution added to it, a white precipitate of silver chloride is formed:

$$KCl+AgNO_3 \longrightarrow AgCl+KNO_3,$$
$$ZnCl_2+2AgNO_3 \longrightarrow 2AgCl+Zn(NO_3)_2.$$

This precipitate is insoluble in nitric acid, but dissolves readily in ammonium hydroxide solution. This reaction will distinguish chlorides from any of the other common salts met with in elementary chemistry.

114. Bleaching-powder, or chloride of lime.—When chlorine is passed into a dilute solution of potassium hydroxide, two salts are formed, potassium chloride and potassium hypochlorite. If the potassium hydroxide concentrated and hot and the chlorine is passed into it in large quantities, the potassium hypochlorite is still further oxidized by the chlorine to form potassium chlorate. This well-known substance is sometimes prepared commercially by this method. Chlorine acts in a similar way on sodium or calcium hydroxide. When chlorine is passed over slaked lime the chlorine is absorbed, and a substance is formed of the composition represented by the formula $CaOCl_2$, and called chloride of lime, or bleaching-powder. If an acid, such as sulphuric acid, is added to this substance, the whole of the chlorine is given off:

$$CaOCl_2+H_2SO_4 \longrightarrow CaSO_4+H_2O+Cl_2.$$

If the acid is quite dilute a large part of the chlorine remains dissolved in the solution, and this liquid acts exactly as does chlorine water.

115. Commercial importance of chlorine and chloride of lime.—Vast quantities of chlorine are required for bleaching cotton and linen, for purifying water, and for disinfecting. The brown appearance of unbleached cotton is known to all, and unbleached linen is still more dingy in appearance. As these fabrics, before they are dyed or stamped, must be made perfectly white, the bleaching industry is important. In the days before the discovery of chlorine the fabrics were sent from all parts of Europe to Holland to be bleached. The process at that time was a very tedious one, continuing for eight months, during which time the cloth went through many operations, in one of which it was spread out in the fields for several months, exposed to the sunlight. Now, thanks to the discovery of chlorine, the whole operation is completed in a few hours. The fabric is first dipped in a solution of chloride of lime, and then in dilute acid. As all of the vast quantities of cotton and linen fabrics have to be bleached in this way, some idea can be formed of the immense quantities of chlorine which are required for industrial purposes. As woollen and silk fabrics are corroded and hardened by chlorine, they cannot be bleached by this agent. Chlorine is a powerful germicide and is used as such in considerable quantities. Thus all the water used by the city of Toronto is chlorinated. Moreover, soldiers, during active service, carry little pellets of chloride of lime, each pellet being of a proper size to sterilize a few gallons of water. In this way typhoid fever was almost eliminated among the soldiers engaged in the Great War.

As chlorine is a very irritating and poisonous gas, workmen greatly dislike working with it in the bleaching rooms, so chloride of lime, rather than the gas itself, is used for this purpose.

116. Manufacture of chlorine.—There are at present three processes by which chlorine is manufactured:

1. *The manganese dioxide process* is the one already described as the best laboratory method for obtaining the gas. Since the manganous chloride produced during the operation is again converted into manganese dioxide, new supplies of the latter reagent are not required for the successive operations.

2. *Deacon's process.* When hydrogen chloride and air are passed through a heated tube, the oxygen of the air combines only very slowly with the hydrogen of the hydrogen chloride. (Sec. 107) Hence little free chlorine passes out, and much undecomposed hydrogen chloride:

$$4HCl+O_2 \longrightarrow 2H_2O+2Cl_2.$$

But heated copper salt acts catalytically and greatly hastens the reaction. In practice, therefore, the hydrochloric acid and air are first heated to 400° C., then they are forced over porous bricks which have been soaked in copper sulphate solution, While passing over the catalyst, about three quarters of the hydrochloric acid liberates its chlorine.

3. *Electrolytic process.* In the United States, where very large quantities of chlorine are now produced, Castner's apparatus is very largely used. Figure 36 is a diagrammatic representation of the apparatus. The stone cell is six feet long, three feet wide, and six inches high. Near each end it has a vertical partition, which does not extend quite to the bottom. A layer of mercury (N) along the bottom forms a seal under the partitions, thus preventing the contents of the various compartments from mixing, and yet forming a conductor between the compartments. The end compartments contain salt solution (V), the central one a dilute

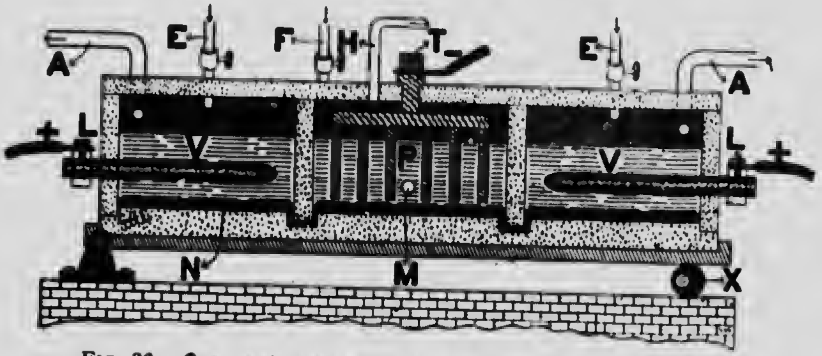


FIG. 36.—CASTNER'S APPARATUS FOR MANUFACTURING CHLORINE AND CAUSTIC SODA

A. Tubes through which chlorine passes off. E. Tubes through which brine enters. F. Tube through which water enters. H. Tube through which hydrogen passes off. L. Positive terminals. M. Opening through which caustic soda is withdrawn. N. Mercury. P. Sodium hydroxide. T. Negative terminal. V. Salt solution. X. Eccentric wheel.

solution of sodium hydroxide (P). The cell is pivoted at one end, and as an eccentric roller (X) rotates under the other, this end is raised and lowered about an inch, thus causing a wave of mercury to pass alternately from each end into the central compartment. While the carbon anodes are in the salt solution, the iron cathode is in the sodium hydroxide solution. When an electric current is passed, chlorine rises from the anodes, and the sodium dissolves in the mercury and, with it, is rocked to the central cell. In the central cell, the mercury acts as an anode; and the sodium appears at the cathode, where it is decomposed by the water, forming sodium hydroxide solution and hydrogen. Chlorine is collected by pipes (A) from the end compartments, and hydrogen (H) from the central compartment. The liquid from the central compartment is withdrawn and evaporated, sodium hydroxide being formed. Thus both chlorine and sodium hydroxide are manufactured by this process. Many other electrical processes, besides that of Castner's, have been invented, and several are used commercially.

It is usual to compress chlorine into a liquid and to store it in iron cylinders. It is from such cylinders that chlorine is discharged in warfare.

QUESTIONS

1. Describe three methods of obtaining chlorine from hydrochloric acid, and two methods of obtaining it from common salt. Write equations.

2. If a printed page has ink stains on it, how can the stains be removed?

3. Can chlorine water be used to remove ink stains from a coloured calico dress? From a piece of white cashmere? From a white silk handkerchief? Give reasons in each case. (Sec. 114)

4. Why does not chlorine bleach printer's ink, and lead-pencil marks? (Sec. 111)

5. When chlorine water is used for testing, why should it be freshly prepared? (Sec. 110)

6. In which would chlorine water keep best, in a clear bottle or in one of amber glass? (Sec. 110) Give reason for your answer.

7. How can chlorine be obtained from common salt? How can chlorine be used to make common salt? How can chlorine be obtained from hydrochloric acid, and how can it be used to make hydrochloric acid?

8. Which of the following substances can be used to dry hydrogen chloride: calcium chloride, quicklime, sulphuric acid? Which of them can be used to dry chlorine?

9. What is the weight of 91 litres of chlorine gas, measured at 20° C. and 586 mm. pressure?

10. How many litres of chlorine at N.T.P. can be obtained from 1000 grams of hydrochloric acid 43 per cent. strong? (Sec. 57)

11. How much hydrogen chloride can be obtained from 1 ton of common salt? If the gas is passed into water to form a 40 per cent. solution (Sec. 57) of hydrochloric acid, what weight of solution will be formed?

12. When 0.461 grams of sodium were burned in chlorine, the resulting chloride weighed 1.17 grams. Find the percentage composition of common salt. If 35.5 is a combining weight of chlorine, find a combining weight of sodium?

13. What weight of antimony must be burned in chlorine to produce 10 grams of antimonous chloride, $SbCl_3$?

14. How can you test a sample of potassium chlorate to find if it contains any potassium chloride as an impurity? Try the potassium chlorate in the reagent bottle.

15. If 1 gram of copper powder is burned in chlorine the powder gains in weight 1.116 grams. What is the percentage composition of copper chloride? What is its simplest formula?

16. When sulphuric acid, sodium chloride, and manganese dioxide are heated together, chlorine is produced. What part is played by each substance in the preparation of the chlorine? Write the equations (Secs. 101 and 107).

17. If 475.5 c.c. of chlorine, measured at 91° C. and 672 mm. pressure, weigh 1 gram, find the molecular weight of chlorine.

18.

Name of substance	Molecular wgt.	Percentage composition			
Hydrogen chloride..	36.5	Hydrogen	2.76	Chlorine,	97.23
Chlorine...........	71.			Chlorine,	100.
Mercuric chloride...	271.	Mercury	73.8	Chlorine,	26.2
Arsenious chloride..	181.5	Arsenic	41.32	Chlorine,	58.68
Stannic chloride....	261.	Tin	45.59	Chlorine,	54.41
Phosphorus chloride.	137.5	Phosphorus	22.55	Chlorine,	77.45

If the substances in the above table were the only known gaseous compounds containing chlorine, find its atomic weight (Sec. 73).

CHAPTER XII

CARBON

117. Occurrence.—The element, carbon, occurs uncombined in several remarkable modifications, of which the best known is the charcoal with which we kindle our fires. But nobody would suspect that the lead of our lead-pencils, much less the beautiful, flashing diamond, transparent as water, consists of the same element as charcoal. Yet both, except for a slight amount of impurity, are composed of carbon alone. In combination with other elements, carbon occurs in several substances, such as the gas, carbon dioxide, which is found in the air, and carbonates, which form great masses of rock in the earth's crust. It is even more important as a constituent of organisms. Not a plant or animal exists, from the humblest organism to man himself, but has every tissue built up of substances containing much carbon. In fact, carbon plays such an important part in the composition of organisms that the chemistry of the carbon compounds is placed in a division by itself, called *organic chemistry*, the chemistry of all the other elements being called *inorganic chemistry*.

118. Modifications of carbon.—(1) *Amorphous carbon* occurs in several forms, of which charcoal is the most familiar. Charcoal is a soft, black, porous substance made from various organic materials, such as wood, sugar, blood, bones, and other refuse parts of animals. Wood charcoal is so light that it floats with ease on water, but this is due to the fact that it is very porous, and each cell, filled with air, acts as a miniature float. When the air is driven out of the charcoal by boiling, it sinks to the bottom of a vessel of water and its true specific gravity of 1.7 is apparent. Again, on account of its many pores, it can present a very large surface to a gas in which it is immersed; and gases tend to condense on and adhere to its surface. We use the term *adsorption* to express this adhesion to the surface of a substance. It is quite a different process from ordinary absorption, such as that of water by wood. In the latter case the water fills the pores of the wood, while in the case of charcoal, the gas simply condenses on the surface of the numerous pores or holes in it. No less than 172 c.c. of ammonia have been adsorbed by 1 c.c. of charcoal made from cocoanut shell, while 68 c.c. of carbon dioxide, or 18 c.c. of oxygen are adsorbed by 1 c.c. of charcoal made from the same material. If, accordingly, foul-smelling gases from sewers or decaying material pollute the air, charcoal, placed near the opening of the sewer, or sprinkled over the decaying organism, will cause the bad odour to vanish. It should be remembered, however, in this connection, that while it adsorbs the odours, it does not destroy the bacteria. Charcoal also adsorbs some colouring materials from solutions. If, for example, charcoal is shaken with litmus solution, and the latter is filtered, the filtrate comes through as clear as water. Indeed, this property is utilized for the clarifying of sugar, as the brown colour is completely removed from the raw syrup by means of charcoal.

Charcoal is insoluble in water and almost all other liquids and is unaffected by most chemicals. Though the most intense heat does not melt it, yet at very high temperatures it turns directly from the solid into vapour.

Charcoal burns readily in oxygen or air, forming carbon dioxide:

$$C+O_2 \rightarrow CO_2.$$

Not only will it unite with free oxygen, but it is capable of removing oxygen from many of its compounds. On this property depends its great value in metallurgy, for the ores of most of the metals can be converted into their oxides by heating them in a blast of air, and if carbon is mixed with the oxide it extracts the oxygen and frees the metal. For example, if red lead, zinc oxide, or copper oxide is mixed with powdered charcoal and heated strongly, the oxide is soon reduced to the metal:

FIG. 37.—OLD METHOD OF PREPARING CHARCOAL
A. Ventilating Shaft

$$Pb_3O_4+2C \rightarrow 3Pb+2CO_2,$$
$$2CuO+C \rightarrow 2Cu+CO_2, \text{ etc.}$$

We shall find later that in some cases the oxide of carbon, which is formed during the reduction of ores, is not carbon dioxide, but another oxide. Only the oxides of a few of the lighter metals, such as sodium, potassium, aluminium, and magnesium cannot be reduced by carbon.

When wood was abundant it was converted into charcoal in the following very wasteful manner: A great pile of cordwood was built compactly (Fig. 37), with a vertical hole at the centre to act as a chimney. The pile was then covered with earth and sods, leaving a few air vents around the base. Next the wood at the bottom was kindled, and by regulating the ventilation properly, the combustion was directed to all parts of the wood. As throughout the operation an insufficient quantity of air was supplied, combustion was incomplete, and almost all of the volatile substances were driven off. Finally the air holes were gradually plugged. After several days, the process of burning being complete, the sods and earth were removed, and a mass of charcoal was obtained which weighed one fourth as much as the original wood. This process is now replaced in Canada by a more scientific one. The wood is heated in iron ovens, and the gaseous substances produced pass through a series of chambers, in which are condensed all the volatile products, such as wood spirits, acetic acid, and wood tar, which all find a ready market. On being heated out of contact with the air, blood, hoofs, bones, and other parts of animals are converted into animal charcoal, which, as it adsorbs the colouring matter, is largely used for clarifying liquids.

Such a method of treating a substance as has just been described, is called *destructive distillation*. During this process the substances are converted by the heat into new products, some of which are volatile and some non-volatile; the former are driven off, while the latter are left behind. On the other hand, in ordinary distillation such as that of a salt solution, the volatile water is driven off as steam and the non-volatile salt is left behind; thus the substances forming the solution are not destroyed, but are merely separated.

When soft coal is destructively distilled the carbon left in the retort is not charcoal, but *coke*. This product, as it is a hard, porous form of carbon, is used for reducing ores. Besides the coke which is left where the coal was placed, a dense form of carbon, called *gas-carbon*, condenses on the sides of the retorts and is used to make carbons for batteries and arc-lamps. Still another form of amorphous carbon is the *lampblack* which, when the wick is turned up, is deposited on a lamp-chimney. It is made on a large scale by the imperfect combustion of fats, resins, and oils. Being in a very finely divided state, it is used for printer's ink, india ink, and black paints. The fact that Roman inscriptions, written on stones with lampblack over two thousand years ago, are still black, indicates how insoluble and how resistant to chemical action is carbon.

(2) *Graphite* has been known for centuries, but was at first believed to contain lead. In 1779, however, Scheele showed that it could be entirely converted into carbon dioxide, and hence must be some form of carbon. Yet it is quite unlike charcoal in its properties; for it is of a steel-gray colour, greasy to the touch, and so soft that it marks on paper. Besides it has to be heated to a high temperature in the air before it ignites; but when it burns it produces carbon dioxide and nothing else.

Charcoal, we have said, is insoluble in most liquids. It does dissolve, however, to a considerable extent in molten iron. When the iron cools part of the carbon appears, but not as charcoal; for it has been converted into layers of lustrous flakes of graphite. Graphite occurs native in many parts of the world, including Quebec and Eastern Ontario, where it is mined. The great graphite mines of the world, however, are in California, Ceylon, and Siberia. It is used as a lubricant instead of oil, especially where bearings become quite hot. It is also largely used, mixed with clay, in the manufacture of lead-pencils.

(3) *Diamond.*—For many ages the diamond has been highly esteemed, both on account of the brilliancy of its fire and on account of its unrivalled hardness. At first, it was believed to be the same substance as rock crystal; but, in 1694, some Italian experimenters placed a diamond at the focus of a powerful lens in sunlight, and were greatly surprised to find that it entirely disappeared.

Fig. 38.—Moissan's Electric Furnace in which he made Diamonds from Charcoal

Its composition was only finally determined when Lavoisier undertook its study. He proved that, when it burned in a closed vessel of air, carbon dioxide alone was produced. The diamond is transparent, and, when pure, colourless; but it is frequently blue, red, or black in colour, owing to impurities. It is the hardest substance known; and, unlike charcoal and graphite, is a non-conductor of electricity.

Fig. 39.—Section of Moissan's Electric Furnace showing the Carbons

Fig. 40.—Artificial Diamonds produced by Moissan in the Electric Furnace

If a diamond is heated strongly in air or oxygen, it takes fire and burns. If, on the other hand, it is heated intensely in an electric furnace, it swells up into a mass of graphite. Moreover, Henri Moissan, the great French chemist, has achieved the reverse process of converting the cheaper forms of carbon into diamonds. To accomplish this he melted iron in an electric furnace (Figs. 38 and 39) and in the molten iron dissolved pure sugar charcoal. When the iron on the outside had solidified he plunged the crucible which contained it into water. Then the contraction of the cooling outer crust produced great pressure on the interior. Finally, the cool iron was dissolved by acid, whereupon a few microscopic diamonds (Fig. 40) were found amongst a large amount of graphite. Up to the present, however, no diamonds of a marketable size have been produced in this manner. India was at first the chief source of diamonds; later Brazil; but now South Africa supplies almost the whole world. Many notable diamonds have been discovered, the most gigantic being the Cullinan diamond, which was found in the Premier Mine, South Africa. It was as large as a man's fist, and weighed one and one-third pounds. Premier Botha's government purchased it and presented it to King Edward the Seventh.

119. Allotropy.—

> "Allotropy is now applied to elements only . . ; for, whereas Berzelius seems to have thought of allotropic forms of an element as existing in different compounds of that element, the modern usage is to confine the term to the various forms of an element which may have been isolated, and have been found to differ in specific gravity, crystalline form, solubility, and other physical properties."
>
> —*Ida Freund*

At first it was not suspected that charcoal, diamond, and graphite all consisted of carbon alone. This was completely proved only when it was shown that one gram of each, when burned, produced 3.67 grams of carbon dioxide, and nothing else. Moreover, as has been stated, charcoal, when dissolved in molten iron, can be converted into graphite and diamond without change of weight; and on the other hand, the diamond can be converted into either charcoal or graphite without change of weight. These facts show us that each of these forms is composed of carbon alone. Different substances, such as these, that are modifications of the same element, are called *allotropes*, and this property is called *allotropy*.

Are these allotropes the same substance, or are they different substances? Is the process of converting one into another, a physical or a chemical change? Undoubtedly, each allotrope has its own specific properties (Sec. 27) quite distinct from those of the others. According to our definition, therefore, each must be considered a pure substance, and the conversion of one into another a true chemical change.

CARBON DIOXIDE

> "Black's account of fixed air (carbon dioxide) and its properties is the first example we possess of a clear and well-reasoned series of experimental researches, where nothing was taken on trust, but everything was made the subject of careful quantitative measurement."
>
> —*Sir William Ramsay, 1900*

120. Preparation.—When any of the modifications of carbon already mentioned are burned, a gas, called carbon dioxide, is formed. In fact, on the burning of any fuel which contains carbon, large quantities of this gas are usually formed. This is due to the combination of the carbon in the fuel with the oxygen of the air:

$$C+O_2 \rightarrow CO_2.$$

Carbon dioxide was first recognized as a distinct gas by van Helmont, a Belgian. The first scientific investigation of its properties and method of preparation was undertaken by Black of Edinburgh, as stated in the quotation at the head of this section.

Van Helmont prepared carbon dioxide by acting on carbonates with acids, and that is still the most suitable method of preparing it for laboratory purposes. The following equations will show the nature of the reaction:

$$CaCO_3+2HCl \rightarrow CaCl_2+H_2O+CO_2,$$
$$Na_2CO_3+H_2SO_4 \rightarrow Na_2SO_4+H_2O+CO_2.$$

Black, on the other hand, obtained the gas by heating carbonates such as those of magnesium and calcium;

$$CaCO_3 \rightarrow CaO+CO_2.$$

Carbon dioxide is produced whenever organic matter ferments or decays. Since fermentation is carried out on an enormous scale in breweries and distilleries, these establishments are able to supply large quantities of this gas for commercial purposes.

121. Physical properties.—Carbon dioxide is a colourless gas, much heavier than air. Its great density can easily be shown; for if two beakers are balanced on the two pans of a balance, and carbon dioxide is poured from a gas bottle into one beaker, the pan of the balance holding this beaker will rapidly drop. It can be condensed by pressure into a colourless, mobile liquid, slightly lighter than water. If the tap of a cylinder containing such liquid carbon dioxide is opened, the liquid issuing from it evaporates so rapidly that the heat which is absorbed causes the liquid to be converted into a white carbon dioxide snow.

122. Chemical properties.—Carbon dioxide dissolves readily in water, 1 litre of cold water dissolving about 1½ litres of the gas. The solution has a sour taste and possesses all the properties of an acid. In conformity with the formulæ of the salts this acid forms with bases, and from analogy with the formulæ of other acids formed by dissolving oxides in water, we say the solution contains an acid of the formula H_2CO_3, called carbonic acid, and consider the reaction,

$$CO_2 + H_2O \longrightarrow H_2CO_3,$$

to take place. Because this oxide unites with water to form carbonic acid, it is called *carbonic anhydride.* It is, nevertheless, impossible to obtain a substance of the formula, H_2CO_3, free from water; if we attempt to evaporate the water from the solution the carbonic acid is entirely decomposed, and the carbon dioxide all escapes:

$$H_2CO_3 \longrightarrow H_2O + CO_2.$$

This solution of carbonic acid in water is an acid, (as has been stated), it turns litmus red, and will react with bases to form salts (Sec. 180). If it is mixed with a solution of sodium hydroxide, sodium carbonate solution is produced:

$$2NaOH+H_2CO_3 \longrightarrow Na_2CO_3+2H_2O.$$

Again, if a carbonic acid solution is mixed with a solution of calcium hydroxide a similar reaction takes place:

$$Ca(OH)_2+H_2CO_3 \longrightarrow CaCO_3+2H_2O.$$

In this last reaction the two clear liquids, when mixed, produce a milky precipitate, as calcium carbonate is insoluble in water. A similar reaction takes place when carbon dioxide is passed into lime-water, and, as this reaction is the test for carbon dioxide, it is worth while to discuss it a little more fully. Slaked lime is calcium hydroxide, $Ca(OH)_2$, a base; lime-water is a solution of this base in water. So, when carbon dioxide is passed into this solution, we can express the reaction as taking place in two stages. First, the carbon dioxide unites with some water to form carbonic acid:

$$CO_2+H_2O \longrightarrow H_2CO_3.$$

And, second, the carbonic acid reacts with the calcium hydroxide to produce calcium carbonate:

$$H_2CO_3+Ca(OH)_2 \longrightarrow CaCO_3+2H_2O.$$

The calcium carbonate, because it is a white insoluble powder, causes the liquid to appear milky; this powder finally settles to the bottom.

Carbon dioxide not only does not support the combustion of wood, a candle, sulphur, or phosphorus, but, if present in the air to the extent of four per cent., it will extinguish a candle. This property, as well as its great density, can be demonstrated as follows: Collect a bottle of the gas by displacement of air, light a candle and bring the mouth of the jar just above and to one side of the flame, and finally, tip up the bottle as in the act of pouring out water; the heavy gas descends on the flame and at once extinguishes it.

123. Physiological effect.—Carbon dioxide is continually exhaled by all plants and animals during respiration. If too great a quantity of it is present in the air an animal suffers through lack of oxygen and may die. Hence, persons descending old wells are sometimes overcome, owing to the presence of the gas in large quantities. In a cave near Naples, sufficient carbon dioxide issues from the fissures in its floor to form a layer from two to three feet deep along the bottom. If a man and a small dog walk through the cave, while the dog quickly becomes unconscious, and soon dies if not rescued, the man, whose head is well above the layer of poisonous gas, feels no evil effects. This cave, on account of its fatal effect on dogs, is called Grotta del Cane, "the cave of the dog".

124. Combustion of magnesium in carbon dioxide.—We usually think of carbon dioxide as a very effective fire extinguisher; yet there are several of the metals that will burn in it. If a bottle of the gas is collected, either over water or by displacement of the air, and a piece of ignited magnesium ribbon, for example, is plunged into it, the metal continues to burn brilliantly. If the products of combustion are examined, it is found that there are little black specks mixed with the white ash, and these can be proved to consist of carbon alone. Again, the white ash has the same properties as the ash formed by burning magnesium in air or oxygen, and is, therefore, magnesium oxide:

$$2\ Mg + CO_2 \longrightarrow 2\ MgO + C.$$

Thus, this experiment proves that carbon dioxide contains carbon and oxygen. Sodium and potassium also burn brilliantly when heated in this gas. This inflammability in carbon dioxide shows that magnesium, sodium and potassium are excellent reducing agents, quite equal to carbon; nevertheless they are not likely to replace carbon commercially for this purpose, as they are too expensive.

CARBON MONOXIDE

125. Preparation.—As one watches the coal burn in a stove a beautiful blue flame is occasionally seen to flicker up; and when coal is added to a fire these blue flames are seen to spread over the whole surface. The gas that produces this flame is carbon monoxide.

If sulphuric acid is added to formic acid, or sodium formate, almost pure carbon monoxide is produced, which, on account of its insolubility, can be collected over water. The reaction depends on the great affinity of sulphuric acid for water; for sodium formate contains both hydrogen and oxygen, and these elements are extracted by the acid from the substance in the proportion in which they are present in water. Then the remaining constituents of the formate combine to form sodium oxide and carbon monoxide:

$$2NaHCO_2 \longrightarrow Na_2O+2CO+H_2O.$$

The sodium oxide further unites with the sulphuric acid to form sodium sulphate. Carbon monoxide can also be formed by the action of sulphuric acid on oxalic acid. In this case, however, the gas is mixed with carbon dioxide; and it is somewhat troublesome to separate the two gases. Hence the method of preparation from sodium formate is better for the laboratory.

For commercial purposes there are two other important methods of preparing carbon monoxide. A piece of iron tubing is filled with granular lumps of charcoal, and the ends are stopped with asbestos corks, each of which has one hole fitted with a glass tube. One glass tube is connected with a flask generating carbon dioxide, while the other glass tube leads to a pneumatic trough in which are gas bottles inverted in water. While carbon dioxide is passing slowly over the charcoal the tube is heated red-hot, and the carbon monoxide formed is collected in the gas bottles. If a pointed tube is inserted in the end of the delivery tube the gas may be ignited. Again, if steam, instead of carbon dioxide, is passed over the red-hot charcoal, a mixture of carbon monoxide and hydrogen is formed. The equations for the reactions are the following:

$$C+CO_2 \longrightarrow 2CO,$$
$$\text{and } C+H_2O \longrightarrow H_2+CO.$$

The mixture of carbon monoxide and hydrogen is called *water gas*, which is manufactured commercially to be used as a fuel. When water gas is manufactured commercially the steam is passed over coal and not charcoal.

126. Properties.—Carbon monoxide is a colourless, tasteless gas, with very little odour. As it is only slightly soluble in water it can be collected readily in the pneumatic trough. The solution is neutral to litmus. The gas burns with a blue flame, producing carbon dioxide. One of its most striking properties is its poisonous character when inhaled. Since it unites with the red part of the blood and thus prevents the latter from absorbing oxygen, the blood cannot be purified. Therefore its inspiration rapidly causes unconsciousness and death. Indeed, it is this component of both illuminating gas and the gas generated in the coal stove which causes these gases to be so injurious when they escape into a room. The formation of carbon monoxide in the coal stove is explained as follows: The oxygen enters below through the grates and at once unites with the red-hot coal to form carbon dioxide. On passing up, however, over more red-hot coal, it is reduced to carbon monoxide, just as was the carbon dioxide when it passed through the red-hot charcoal in the iron tube. When this carbon monoxide reaches the space above the coal it again combines with oxygen, re-forming carbon dioxide and giving rise to the blue flames already mentioned.

127. Hydrides of carbon.—While carbon ordinarily combines with oxygen in only two proportions to form the two oxides described already, it combines with hydrogen in many proportions to form many hydrides. If the properties of these hydrides are compared, it is found that they form a number of series. The members of each series have closely related formulæ; and if the members of each series are arranged in the order of their boiling-point, it is found that they are in the right order to exhibit a steady gradation of many other properties as well. The following list contains the names and formulæ of some members of three of these series:

The Methane Series		*The Ethylene Series*		*The Acetylene Series*	
Methane,	CH_4	Ethylene,	C_2H_4	Acetylene,	C_2H_2
Ethane,	C_2H_6	Propylene,	C_3H_6	Allylene,	C_3H_4
Propane,	C_3H_8	Butylene,	C_4H_8	Crotonylene,	C_4H_6
Butane,	C_4H_{10}	Amylene,	C_5H_{10}		
Pentane,	C_5H_{12}	Hexylene,	C_6H_{12}		

It will be noticed that the formula of each member of a series is formed from the formula of the preceding member, by adding CH_2 to it.

The members of the methane series of lowest molecular weight are gases, the middle members are liquids, and the members of highest molecular weight are solids. The boiling-points of the members rise as we descend the series. Petroleum is composed largely of members of this series. The members forming petroleum are separated by heat, the components that boil at low temperatures being driven off at low temperatures, and then those that boil at higher temperatures. The components that boil between 40°C. and 70°C. form *petroleum ether*, those between 70°C and 90°C *gasolene* (refined), between 150°C and 300°C *kerosene*. The components of the petroleum which boil above 300°C form *lubricating oils*, *vaseline*, and *paraffin*.

We will discuss briefly the first member of the first series, methane, and the first member of the third series, acetylene.

METHANE, OR MARSH GAS

128. Occurrence.—If the decaying vegetation at the bottom of stagnant water is stirred with a stick, bubbles of gas will frequently be seen to rise. In some marshy places these bubbles rise steadily, even when the bottom is not disturbed. If an inverted bottle, full of water, is placed so as to catch the bubbles, a bottle of the gas may be collected, which burns much like hydrogen when a blazing splint is brought to the mouth. This gas is *methane*, or *marsh gas*. It is formed whenever vegetation decays under water.

129. Preparation.—Methane can be obtained most readily by the action of water on aluminium carbide. The carbide is placed in a flask (Fig. 4) fitted with a cork with two holes. Through one hole a separating funnel is passed, and through the other an elbow tube connected with a rubber delivery tube. Water is allowed to drop on the carbide from the separating funnel. The gas is collected over water:

$$Al_4C_3+6H_2O \longrightarrow 3CH_4+2Al_2O_3.$$

130. Properties.—Methane is a colourless, odourless gas, which is only half as heavy as air. It dissolves very sparingly in water. It burns with a slightly luminous flame, producing carbon dioxide and water:

$$CH_4+2O_2 \longrightarrow CO_2+2H_2O.$$

It can be distinguished from hydrogen by the fact that, when a bottle of it is burned and lime-water is poured into the bottle and agitated, the liquid turns milky. It can be distinguished readily from carbon monoxide by the fact that, when it is burned from a jet, a cold, dry jar held over the flame condenses drops of water on the inside.

Methane is given forth from coal, and so occurs in large quantities in coal mines. Indeed, sometimes it so permeates coal that, when a seam is cut through, it can be heard to hiss out. The colliers have named such coal, singing coal, and the gas, *fire-damp*. If the gas becomes ignited in a mine a terrific explosion occurs. The explosion is due to the sudden expansion of the carbon dioxide and steam formed as products of its combustion. Many thousands of miners have lost their lives through such explosions; for not only are they cut off by the blocking of the passage ways, but they are also suffocated through lack of oxygen and through the great quantities of carbon dioxide produced. The vitiated air is called *after-damp*. A thorough system of ventilation and the use of electric lighting and safety lanterns are the best methods of preventing such explosions.

ACETYLENE

131. Preparation.—Acetylene is prepared in a manner exactly similar to methane, excepting that water is dropped on calcium carbide instead of on aluminum carbide. A simpler laboratory method, however, is to drop a lump of the carbide into water and to place an inverted gas bottle filled with water in such a position as to receive the gas as it ascends. The reaction is expressed by the following equation:

$$CaC_2+2H_2O \longrightarrow Ca(OH)_2+C_2H_2.$$

If the liquid which remains after acetylene has been formed from calcium carbide and water, is filtered, the filtrate, if the breath is blown through it, turns milky at once. This proves that calcium hydroxide is one of the products of the reaction. The blackish parts which remain on the filter paper are impurities present in the calcium carbide.

132. Properties.—Acetylene is a colourless gas with a characteristic odour. Water dissolves about its own volume of the gas, alcohol dissolves six times its own volume, but *acetone* dissolves it in much larger quantities. The gas burns with intense heat and light, producing water and carbon dioxide if the supply of oxygen is ample, but depositing much carbon if the supply of air is insufficient:

$$2C_2H_2+5O_2 \rightarrow 4CO_2+2H_2O.$$

As two volumes of acetylene require five volumes of oxygen, and only one fifth of the air is oxygen, therefore acetylene requires about twelve times its volume of air for complete combustion. Acetylene is liable to explode if it is compressed under a pressure of more than two atmospheres, especially if subjected to any shock.

133. Economic importance.—Acetylene gas is now an article of great commercial importance. A plant for its generation is not expensive and is easily managed. Consequently, where coal-gas is not accessible, many houses and public buildings have installed private acetylene plants and use the gas for illumination and cooking. It is also largely used with oxygen, in the oxy-acetylene blow-pipe, for cutting iron plates (Sec. 17), and for autogenous welding. As it is not safe to store the compressed gas in cylinders, it is generally used dissolved in acetone. These solutions in acetone are contained in cylinders. In this form it is used for lighting automobiles. When the cylinders become exhausted they are returned to the factory to be recharged.

COAL-GAS

134. Manufacture of coal-gas.—Almost every large town and every city has a supply of coal-gas, which is used for purposes of cooking and of illumination. It is produced by the destructive distillation (Sec. 118) of soft coal. Fig. 41 shows the arrangement of the parts of a gas plant. The coal is placed in fire-clay retorts (R), which are heated in a furnace. The gases produced are partially condensed in a large pipe, the hydraulic main, one of which is usually connected with several furnaces. The gases not condensed here are passed into tall pipes (C), where they are further cooled and a further condensation of liquids takes place. The gases are then pumped into large towers called "scrubbers" (S), where they meet a stream of water trickling down over masses of coke. This water dissolves all the ammonia from the gases, which then pass through the purifier (P), where other unsuitable components are absorbed. Finally the gases pass into the gas-holders (H). The liquids that are condensed in the hydraulic main and in the condenser form a black mass called coal-tar, which is used for a variety of purposes.

The solid left in the retort is coke. Hydrogen and methane compose between seventy and eighty per cent. of the gases in the gas-holders.

Coal-gas was first manufactured for practical use by William Murdoch, a Scotsman, who used it to illuminate his home in 1792. By 1805, it began to be used for the illumination of large buildings. Its use for street lighting spread rapidly in cities; but at the present time, in Ontario, it bids fair to be largely replaced by electricity for illumination and also for heating and cooking.

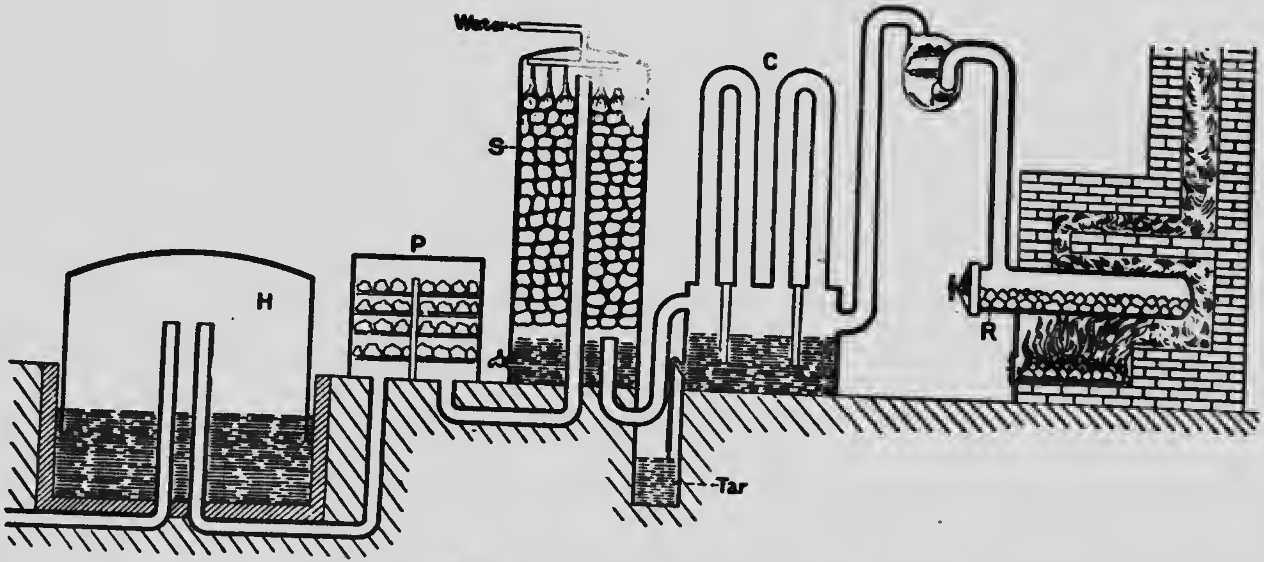


FIG. 41.—DIAGRAM OF PLANT FOR THE MANUFACTURE OF COAL-GAS

R. Retort in which the coal is placed. C. The condensers in which tar collects. S. Scrubbers in which the gas is washed by water. P. Purifiers in which the hydrogen sulphide is removed. H. The gas-holder.

QUESTIONS

1. Name and describe the different forms of carbon. How may they be shown to be the same element?

2. What is meant by allotropes? How would you prove that two substances are allotropes of the same element?

3. How would you distinguish carbon monoxide, methane, and hydrogen?

4. Name four methods by which carbon dioxide is formed. Write equations.

5. Roscoe, by burning 6.4406 grams of diamond, obtained 23.7114 grams of carbon dioxide and nothing else; while Dumas, by burning 1.232 grams of graphite, obtained 4.517 grams of carbon dioxide and nothing else. Prove from these data that diamond and graphite are allotropes of carbon (Sec. 19).

6. When 39 c.c. of carbon monoxide are exploded with 24 c.c. of oxygen, what volume of these gases is left? What is the composition of the residual gases?

7. If 10 grams of pure charcoal are burned in oxygen, what volume of oxygen is required; and what weight, and what volume of carbon dioxide are produced?

8. Into a eudiometer are bubbled 20.2 c.c. of carbon monoxide. Oxygen is then bubbled in, until the gases stand at 40 c.c. After the explosion, what volume will the resulting gases occupy? If potassium hydroxide (Sec. 122) solution is shaken with the gases, what volume of gases will then remain?

9. How would you show that sugar, starch, cheese, and diamonds contain carbon?

10. How would you prove that carbon dioxide contains both carbon and oxygen? (Sec. 124)

11. Explain how carbon monoxide is formed in a coal stove, and state why it is dangerous to allow it to escape into the room?

12. Why is it customary to lower a lighted candle into a well to find if it is safe for men to descend into it?

13. If oxalic acid is heated with sulphuric acid, a mixture of carbon monoxide and carbon dioxide is given off. How can you obtain pure carbon monoxide from the mixture? On what properties of the gas does the separation depend?

CHAPTER XIII

ECONOMIC IMPORTANCE OF CARBON DIOXIDE AND CARBONATES

135. Soda-waters.—Such beverages as ginger-ale, ginger-beer, and soda-water are well known. All are usually kept in thick glass bottles. When the cork is withdrawn from a bottle and the liquid is poured into a glass, violent effervescence occurs. The essential components of all these beverages are water and carbon dioxide; the gas is forced into the bottle under pressure, and the bottle is then corked. As the solubility of a gas decreases with a decrease of the pressure, much of the carbon dioxide escapes from a bottle of soda-water when the bottle is opened and the pressure diminished. The carbonic acid dissolved in the liquid gives these drinks their sharp taste. The various flavours and colours are produced by extracts, and the beverages are generally sweetened by sugar. Ginger-beer is different from the others in this, that carbon dioxide is not forced into it but is produced by the fermentation of ginger in the liquid itself.

136. Fire extinguishers.—In halls and corridors of public buildings are placed small metal tanks called fire extinguishers, each of which has a short piece of hose and a nozzle (Fig. 42). The tank is filled with a strong solution of sodium bicarbonate, and in the top is a stoppered bottle of sulphuric acid. The printed instructions on each state that, in case of fire, the tank should be inverted and the nozzle directed toward the fire.

The act of inverting the extinguisher withdraws the cork or breaks the bottle, and the acid then reacts with the carbonate to generate carbon dioxide:

$$H_2SO_4+2NaHCO_3 \longrightarrow Na_2SO_4+2CO_2+2H_2O.$$

The carbon dioxide rises to the space above the liquid, forces the latter out through the hose, and then this liquid extinguishes the fire.

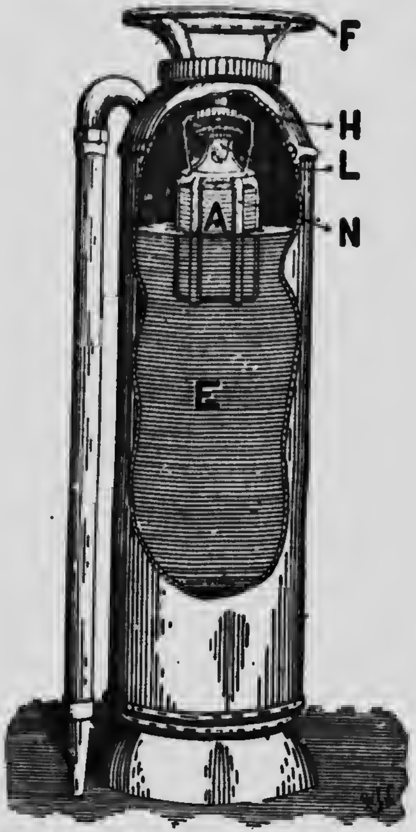


FIG. 42.— FIRE EXTINGUISHER WITH PART OF SIDE CUT AWAY

A. Bottle containing sulphuric acid. E. Metal cylinder containing a strong solution of sodium bicarbonate. F. Handle for carrying extinguisher. H. Bracket to catch lead stopper when extinguisher is inverted. L. Lead stopper fitting loosely into the neck of the bottle. N. Suspended frame for supporting the bottle.

137. Making of lime.—When limestone is strongly heated it is decomposed into quicklime and carbon dioxide:

$$CaCO_3 \longrightarrow CaO+CO_2.$$

It can be proved that quicklime is an oxide of calcium, for, when the metal, calcium, is burned in air or oxygen, a substance identical in properties with quicklime is produced. The process of converting limestone into lime is called burning lime, though, in reality, the lime is not burnt, but strongly heated. As vast rock formations of limestone are found at or near the surface in many parts of Canada, the making of lime is an important industry. Lime is produced in a structure called a lime-kiln (Fig. 43), which is a conical shaft open at the top and with a furnace near the bottom. The limestone is carried in little cars on an elevated track to the top of the shaft and is dumped into the kiln. As soon as the limestone at the bottom is calcined, it is taken out from below and the upper limestone gradually drops down.

FIG. 43.—SECTION OF A LIME-KILN OF SIMPLE FORM

Quicklime, when water is added to it, swells up, cracks, and steams as it becomes heated. When the process is complete, the hard quicklime has been converted into a white crumbling powder, *slaked lime*, or calcium hydroxide:

$$CaO + H_2O \longrightarrow Ca(OH)_2.$$

The same reaction also occurs when quicklime is exposed to water vapour, and for this reason it is sometimes used as a drying agent for gases. At ordinary temperatures the reaction that takes place in the lime-kiln is reversed; in other words, both quicklime and slaked lime, if exposed to the air, will rapidly deteriorate by changing to calcium carbonate. Indeed, it is to this reaction that the hardening of lime-mortar is due.

138. Solubility of limestone.—We have seen that, when carbon dioxide is passed into lime-water a white precipitate of limestone is produced, which is quite insoluble in water. However, if more carbon dioxide is passed into the liquid, the limestone dissolves. Similar results can be obtained by adding a solution of carbon dioxide (soda-water) to the precipitate. Hence limestone is soluble in water in which carbon dioxide has been dissolved. This fact is of great importance in the economy of nature. For, as decaying vegetation always produces carbon dioxide, the water of rivers and springs contains small amounts of this gas; and, if this water flows over limestone, the latter is gradually dissolved. We say such water contains "lime", but it is really not lime, but limestone that it has dissolved. By the flow of such streams great caverns and underground passages are produced in the limestone rocks.

139. Hard and Soft Water.—We classify water as hard or soft, and the two kinds have well-marked differences. Hard water feels rough and resistant to the touch, while soft water feels smooth. When a small amount of soap solution is added to hard water, a white cloudy precipitate is formed, which, being lighter than water, soon floats on the top. Moreover, no lather is produced at first when the solution of soap is shaken with the water. Soap when added to perfectly soft water, even in small quantities, produces a lather at once when the water is shaken. The hardness of water is due to the presence of calcium and magnesium salts, especially the carbonates, chlorides, and sulphates. Now, soap is the sodium or potassium salt of acids obtained from fats, one of these being oleic acid. Hard soap contains sodium oleate and soft soap contains potassium oleate. If either kind of soap is added to water containing a calcium or a magnesium salt, calcium or magnesium oleate is formed; and, as these are both insoluble in water, they form precipitates, which are the curds produced in hard water by soap. Accordingly, the soap is destroyed and does not perform its function as a cleanser. As a consequence, only after enough soap has been added to precipitate all the calcium salt, does any become available as a cleanser. In this way millions of pounds of soap are wasted every year by the use of hard water.

If sodium carbonate or ammonium carbonate is added to the hard water, the reactions expressed by the following equations take place:

$$Na_2CO_3+CaCl_2 \longrightarrow 2NaCl+CaCO_3,$$
$$Na_2CO_3+MgCl_2 \longrightarrow 2NaCl+MgCO_3.$$

The calcium and magnesium carbonate produced are insoluble in water and sink to the bottom; thus, when soap is added, a lather is at once produced, as no salts of calcium and magnesium are left dissolved in the water. Sodium and potassium salts dissolved in water do not precipitate the soap, and so do not make water hard. It is because sodium carbonate softens water by precipitating the calcium and magnesium salts that it is called *washing-soda.*

Sodium carbonate is also added to water on account of its cleansing properties. It acts readily on any oil or grease on the surface, converting it into soap.

Rain and distilled water are soft. Spring water is usually very hard, as it is certain to have dissolved some calcium or magnesium salts during its long passage through the soil and rocks. The hardness of river water varies greatly on account of the varying soils and rocks through which it flows.

140. Temporary and permanent hardness.—It can be shown that a solution of carbon dioxide dissolves limestone and also magnesium carbonate. When such a solution is heated, as the carbon dioxide is driven off, the water is no longer able to dissolve the carbonates, and they are precipitated. It is in this way that the deposit of "lime" forms inside kettles and boilers. If water containing much "lime" is heated, a cloudiness is produced, owing to the precipitation of the calcium or magnesium carbonate. Consequently, water that is hard owing to the presence of these carbonates, can be made soft by boiling, and is, therefore, said to possess *temporary hardness*, while water containing the chlorides or sulphates of calcium and magnesium is said to possess *permanent hardness*.

141. Baking-soda, baking-powder, and yeast.—Bread is made light by adding yeast, which, by causing carbon compounds in the dough to ferment, generates carbon dioxide. The carbon dioxide collects throughout the mass as numerous small bubbles, making the dough porous and causing the bread to rise. As the bread bakes the dough hardens, and finally retains its shape even when the gas escapes. Yeast does not produce carbon dioxide very rapidly and would be altogether too slow for making cakes, etc. For this purpose baking-soda and baking-powder are used. The former is sodium bicarbonate, $NaHCO_3$, which, when heated, produces carbon dioxide and sodium carbonate:

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O.$$

It will be observed that only one half of the carbon dioxide obtainable is thus driven off, for it is possible to obtain still more carbon dioxide by adding an acid to sodium carbonate. In order to utilize all the carbon dioxide available, therefore, the sodium bicarbonate is usually mixed in proper proportions with a substance that acts like an acid. Such a mixture is called *baking-powder*. The added substance is usually cream of tartar, alum, or acid calcium phosphate. Usually some starch is mixed with the two essential ingredients, thus forming a layer around the particles of the other components and preventing them from coming into contact and reacting. No matter what acid substance is used, a salt is left behind in the dough, and it is essential that this should be harmless. Probably the cream of tartar baking-powder is the best. There is a prevalent opinion that alum is very injurious in baking-powder, but there is some doubt as to the truth of this.

QUESTIONS

1. Explain how yeast causes dough to rise.

2. Why do bread and cakes rise greatly after they are placed in the oven?

3. A vessel of water, saturated with carbon dioxide under ordinary pressure, is placed under the receiver of an air-pump and exhausted. Describe what happens to the solution. Why does spring water sometimes deposit limestone when it reaches the surface?

4. Water that has temporary hardness and cannot be heated on account of the large quantity to be treated is softened by adding some lime to it. Explain how this softens it, and write the equation expressing the reaction.

5. Sour milk is sometimes used with baking-soda in cooking. Would sweet milk do as well? Give reasons for your answer.

6. Write the equations for the action of sulphuric acid on sodium carbonate and on sodium bicarbonate. From the equations decide which carbonate requires more acid to liberate the carbon dioxide from it. State one reason why it is advantageous to use the bicarbonate rather than the carbonate in baking-powder.

7. How can you prepare lime-water, if you are given a piece of marble?

8. If 1,000 kilograms of limestone is placed in a lime-kiln and heated, how much quicklime will it produce? What volume of carbon dioxide, measured at N.T.P., will be driven off?

9. Sodium carbonate occurs in crystals $Na_2CO_3 \cdot 10H_2O$, and as a white powder Na_2CO_3. If both are sold at the same price per pound, which will be the more profitable to purchase?

10. What weight of water is necessary to slake 1 ton of lime?

11. A mixture of marble and hydrochloric acid sets carbon dioxide free. Why can you not use this mixture instead of baking-powder?

CHAPTER XIV

CHEMICAL ACTION

142. Heat of chemical action.—Up to the present we have confined our attention entirely to the substances that are formed during a chemical action and have not paid much attention to the phenomena accompanying the action. Some chemical changes, such as the burning of magnesium in air or the slaking of lime, are accompanied by the production of great heat; others, such as the rusting of iron or the bleaching of cloth by chlorine, take place with little or no evidence of heat production; in others, again, such as the conversion of limestone into lime or the decomposition of mercury oxide into mercury and oxygen, heat, instead of being produced, is taken up during the reaction. If the rusting of iron and the bleaching of cloth are examined more carefully, it is found that heat changes accompany them also, though the changes take place so slowly that the heat is dissipated before it has time to elevate to any extent the temperature of the iron or of the cloth. In fact, every chemical reaction is accompanied by the production or absorption of heat. Reactions in which heat is absorbed are called *endothermic*, while those in which heat is emitted are *exothermic*. Many examples of each kind have been met already. The burning of any substance affords a good example of an exothermic reaction, while those changes that are brought about only by strong heating, such as the production of oxygen by decomposing mercury oxide, manganese dioxide, and saltpetre, are often endothermic. It does not follow, however, that all reactions that require the aid of heat are endothermic, for some, as, for example, the calcining of the metals and the decomposition of potassium chlorate, that require the application of heat to bring them about, are exothermic.

Moreover, when two or more elements combine to form a compound the reaction is accompanied by the absorption or emission of heat. In such cases, if heat is emitted the compound is called an *exothermic substance*, but if heat is absorbed it is called an *endothermic substance*. Usually endothermic substances are much less stable than exothermic ones; indeed, frequently they decompose spontaneously, sometimes with explosive violence. Most of the compounds met with in elementary chemistry are exothermic, but acetylene, hydrogen iodide, and several oxides of nitrogen are examples of endothermic substances.

143. Speed of reactions.—Every pupil must have noticed the various speeds at which reactions take place. While a piece of wood burns slowly, a piece of magnesium ribbon of the same length burns much more rapidly. Again, a piece of charcoal burns slowly in air but rapidly in oxygen. Several factors determine the speed.

(*a*) *Temperature* is a very important factor in determining the rate of a reaction. Many of the reactions we have studied do not seem to take place at all at an ordinary temperature, but only as the temperature is raised. If sulphuric acid is poured upon common salt (Sec. 101) and the containing vessel is kept cool, the hydrogen chloride comes off gently; but if the temperature is raised, the gas comes off in torrents. And what is true in this case is equally true in many others, for the rate of all reactions increases from two to three times for every 10° C. the temperature is raised. At the temperature of the flame from a Bunsen burner coal burns in air quite readily; but as the temperature is lowered, the rate decreases very rapidly, so that at ordinary temperatures there is apparently no action at all. Yet reactions that take place at high temperatures may take place at ordinary temperatures also, but at such a slow rate that no perceptible change is noticeable even after years. In the case of coal, for example, while we usually consider that no combustion takes place while it is in the bin, yet we know that great masses of coal sometimes ignite spontaneously in their interior. In such a case, the heat of oxidation gradually accumulates until the coal finally ignites. Hence, large piles of coal require to be flooded with water occasionally, or to be ventilated, to prevent spontaneous combustion.

(*b*) *Catalysts* are also a means of changing the speed of reactions. We have had several examples of this already. It is now generally considered that a catalyst cannot initiate a reaction, but that it can merely accelerate one that is already taking place. The rate at which carbon monoxide unites with oxygen, even at a high temperature, is so slow when both are perfectly dry that no apparent action takes place; but as soon as moisture is admitted, the reaction takes place with great rapidity. Now, as far as experiment indicates, there is no reaction until the catalyst, moisture, is added to the mixture of carbon monoxide and oxygen; but according to the usual explanation of catalytic action, there is considered to be already an exceedingly slow reaction, the rate of which the catalyst merely increased.

Catalysis is of great industrial importance; for many of the most important commercial processes of a chemical character depend entirely upon it for their success. By the use of a catalyst the price of the most extensively used of all chemicals, sulphuric acid, was reduced from several dollars a pound to less than one cent. Again, much of the chlorine, now so widely used, is separated from hydrogen by copper salts acting as catalysts (Sec. 116). The processes of fermentation, also, that are so far-reaching in industry, are catalytic reactions.

But if catalysis plays a large part in the phenomena of the industrial world, this is as nothing compared with the part it plays in the life of organisms of all kinds from the smallest bacteria to man himself; for from the time the food enters the mouth until it is absorbed into the blood, the chemical processes it undergoes are largely catalytic. Besides, the chemical processes of the various tissues are also largely of a catalytic nature. Accordingly, a clear understanding of this process is of transcendent importance in understanding the phenomena of life.

(*c*) *Area of surface in contact* also plays a prominent part in determining the speed of a reaction. Two substances react only where they are in contact. If a lump of zinc is dropped into sulphuric acid, as only the layers of zinc and sulphuric acid that are in contact can play any part in the chemical reaction, the internal parts of the zinc affect the reaction no more than does the great mass of the acid which does not touch the metal. Accordingly, if a lump of zinc is dropped into acid, the rate is just the same, whether the lump is hollow or solid. Thus the greater the surfaces in contact the greater is the speed. For example, if two lumps of marble of equal size are selected, and one is ground to a fine powder while the other is left intact, and if both are immersed in sulphuric or hydrochloric acid, the action of the acid will be very much more rapid on the powder than on the lump, because the surface of the powder is many times that of the lump. A lump of iron does not appear to be acted on at ordinary temperatures by the oxygen of the air, yet if this metal is prepared in the form of a very fine powder, by a special method, and the powder sprinkled out into the air, it ignites with as great vigour as does antimony in chlorine. Moreover, several other metals, such as lead, nickel, and cobalt, act in the same manner. In such cases the rate has been increased by the immense increase of the surfaces in contact.

(*d*) *Concentration.* By the concentration of a substance is meant the amount of it per unit volume, the term being applied either to a gas or to a dissolved substance. The rate at which a gas or dissolved substance reacts increases with its concentration, as is obvious from a consideration of the following well-known facts: To hasten the hardening of plaster and mortar in new buildings by absorption of carbon dioxide, braziers of burning coke are frequently placed near the walls, in order to increase the concentration of this gas in the air. For the same reason, in addition to the reason given in Section 16, sulphur and other combustibles burn more rapidly in pure oxygen than in air, in which the oxygen is diluted five-fold with nitrogen. Moreover, a concentrated solution of chlorine in water bleaches more rapidly than a weak one, and marble is acted on more rapidly by concentrated acids than by weak ones, as shown by the more vigorous evolution of carbon dioxide. In photography also the effect of concentration on the speed of reaction plays an important rôle, for, by a careful adjustment of the concentration of the chemicals in the developer, the photographer is able to regulate to a nicety the time required to develop his plates and films.

144. Reversible reactions and chemical equilibrium.—We are now in a position to explain certain chemical reactions which have already been studied separately, but which when studied together seem contradictory. One method of preparing hydrogen is by passing steam over iron heated red-hot in a combustion tube (Sec. 41):

$$3Fe+4H_2O \longrightarrow Fe_3O_4+4H_2.$$

Now, if the very same tube, with the same filings partially oxidized to oxide of iron, is heated and hydrogen is passed through it, the iron oxide is reduced to iron, and the hydrogen is oxidized to water:

$$Fe_3O_4+4H_2 \longrightarrow 3Fe+4H_2O.$$

If the equations expressing the two reactions are compared, it will be found that they are exact opposites. How is this to be explained?

Before we explain this apparently contradictory behaviour, let us consider what would take place if water and iron were sealed in a glass tube and heated. As the iron became hot and the water turned to steam the first of the foregoing reactions would begin. The iron would liberate the hydrogen, and the velocity of the reaction would depend on the temperature and the concentration of the gas (steam), as the concentration of solids remains unchanged. When the temperature becomes steady, the only variable feature will be the concentration of the steam in the tube. As the reaction proceeds the amount of steam decreases, and thus the velocity of this reaction will become slower. But as soon as this reaction begins and some hydrogen and iron oxide are formed, the second of the foregoing reactions will also begin. At first, as the concentration of the hydrogen is very small, this latter reaction is very slow; but, as the first reaction proceeds, more hydrogen is produced, and the rate of the second reaction will increase. Thus the rate of the first reaction is steadily decreasing, and the rate of the second is just as steadily increasing, so that in time the rate at which hydrogen separates from the water is the same as that at which it is uniting with the oxygen of the iron oxide to form water. Then the amounts of each substance in the tube will not change, as each one is being formed at the same rate as that at which it is being destroyed. Of course, it is not necessary to assume that these two reactions are really taking place simultaneously. The observed fact is that a state of rest or *chemical equilibrium* has been reached. Since by a slight alteration of concentration the process may be made to take place in one or the other direction, such a reaction is spoken of as a *reversible reaction*. Reactions of this kind are expressed by equations with double arrows, thus:

$$3Fe+4H_2O \rightleftarrows Fe_3O_4+4H_2.$$

When steam passes over iron, the former is reduced, and hydrogen is produced, there seemingly being no decrease in the rate, as the apparatus will deliver hydrogen as long as there is any unoxidized iron. Here there is no decrease in the rate of the reaction for, quite unlike the case of the sealed tube, there is no decrease in the concentration of the steam, because new steam is being continually supplied. Why does not the reverse reaction increase and counterbalance this reaction? Because there never is any concentration of hydrogen in contact with the iron oxide. For as soon as the hydrogen is formed, it is swept out of the tube with the current of steam. Thus the second reaction is always exceedingly slow, because there is no concentration of hydrogen. When, on the other hand, hydrogen is passed over iron oxide to form steam, the latter is swept away as rapidly as it is formed, and thus the hydrogen will continue to reduce the oxide as long as it passes through the tube. In this way the reaction can be made to go completely in either direction, by keeping up the concentration on one side and keeping it down on the other.

Let us consider further the reaction expressed by the equation,

$$3Fe+4H_2O \rightleftarrows Fe_3O_4+4H_2,$$

where the substances are inclosed in a sealed tube. At 200°C. a state of equilibrium is reached, when there is 20 times as much steam as hydrogen. Now, if the temperature is raised and thus the speed of reaction in each direction is increased, it will be found that the speed of the reaction from right to left has increased more rapidly than that from left to right, and that in the equilibrium state at 440°C. the amount of steam is only 6 times as much as that of hydrogen, while at 1,500°C. the amounts of steam and of hydrogen are equal. If such a reaction is produced in a closed vessel, the changes take place in one direction as the temperature is raised and in the opposite direction as the temperature is lowered, so that the reagents at the end of the operation will be present in exactly the same quantities as at the beginning.

We have found that when mercury is heated in air it forms red oxide:

$$2Hg+O_2 \longrightarrow 2HgO;$$

and that if the temperature is raised, the reverse reaction takes place completely:

$$2HgO \longrightarrow 2Hg+O_2.$$

Both the reactions are apparently complete. At the lower temperature the latter reaction takes place at such an infinitely slow rate that the former appears complete. But with rise of temperature the rate of decomposition of the mercury oxide increases much more rapidly than the reverse process, so that at high temperatures the rate of combination—which is never great—is negligible when compared with the rate of decomposition.

145. Reactions complete in one direction.—Most chemical reactions are purposely arranged so that they will not come to a state of equilibrium where there will be a mixture of all the substances taking part in the reaction, for such substances would be difficult to separate, and the purpose of most experiments is to isolate substances. Thus reactions, to be useful, must be fairly complete in one direction. This is accomplished mainly by the production of an insoluble substance, which usually is either a gas which rises out of the solution or a solid which is precipitated.

As an example of the first, consider the preparation of hydrogen chloride:

$$H_2SO_4+NaCl \rightleftarrows NaHSO_4+HCl.$$

This reaction can be made reversible, but, if the mixture is heated, the hydrogen chloride gas is driven off. Consequently, its concentration in the sulphuric acid is always so small that the reaction from left to right goes practically to completion, as the rate from right to left is exceedingly slow on account of the very small concentration of hydrogen chloride in the solution.

As an example of the second method, consider the action of a solution of silver nitrate on a solution of common salt:

$$AgNO_3+NaCl \rightarrow NaNO_3+AgCl.$$

Here all of the substances are quite soluble in water except the silver chloride. The reaction begins from left to right, as at first there is no sodium nitrate or silver chloride in the solution. Now it might be thought that as these two latter are formed they would begin reacting in the opposite direction; and such would be the case if both were soluble; but, because silver chloride is insoluble, its concentration in the solution remains practically zero. Hence the rate of reaction from right to left remains nothing, and the reaction is complete in the opposite direction.

The same reasoning always applies where an insoluble substance is formed. If A+B⟶C+D represents a reaction, and if C or D is either a gas that escapes, or, when the reaction takes place in solution, an insoluble solid or liquid, the reaction takes place practically completely from left to right. If all of the reagents are soluble and in equilibrium, then any increase in concentration of A or B, or any decrease in concentration of C or D will cause the equilibrium to be displaced, so that more of C and D will be formed, and vice versa. The pupil should study the chemical reactions already described in this volume and decide whether they were complete in one direction, or in a state of equilibrium, and determine the factors that made them complete or incomplete.

146. Disturbance of equilibrium.—When a reaction is in a state of equilibrium, this state can be disturbed in several ways: (1) By changing the concentration or active mass of any of the substances involved in the reaction; (2) by changing the temperature; or (3) by changing the pressure of the substances involved. But the question arises in which direction the equilibrium will be displaced. The conversion of calcium carbonate into lime and carbon dioxide, if conducted in a sealed tube, comes to a state of equilibrium:

$$CaCO_3 \rightleftarrows CaO+CO_2.$$

It is important to know in which direction equilibrium will be displaced if any of the factors mentioned above should be altered.

Le Chatelier has formulated a rule by which in every case one can tell in an instant in which direction equilibrium will be displaced. His rule is as follows: *When one or more of the factors determining an equilibrium are altered, the equilibrium becomes displaced in such a way* *as to neutralize, as far as possible, the effect of the change.* This rule is called *Le Chatelier's Theorem.*

Let us apply this rule to the mixture of limestone, lime, and carbon dioxide in a state of equilibrium in the sealed tube. Suppose more carbon dioxide is forced into the tube and thus its concentration is *increased*, then the equilibrium of the mixture will be displaced in such a direction as to *decrease* the concentration of the carbon dioxide. The way to decrease the concentration of the carbon dioxide, when more is being forced in, is to get rid of carbon dioxide, and so the substance on the left will be produced, more limestone being formed. If carbon dioxide is withdrawn from the tube, the reaction will take place from left to right, in order to generate more carbon dioxide. If the temperature is *raised*, the equilibrium will be displaced in the direction that causes the absorption of heat, for this leads to a lowering of *the temperature;* hence the substances on the right will be produced, as this reaction is accompanied by heat absorption. If the pressure is *decreased*, then more carbon dioxide will form to *increase the pressure* of the gas, and the reaction will be displaced from left to right. In a similar way this rule is applied to all balanced chemical reactions.

QUESTIONS

1. Classify the following reactions as complete or incomplete, giving reasons :
    - (*a*) Potassium chlorate is heated to produce oxygen.
    - (*b*) Sulphuric acid is added to sodium chloride.
    - (*c*) The mixture in (*b*) is heated.
    - (*d*) Sodium is placed on water.
    - (*e*) Hydrogen and oxygen are passed through a highly heated tube.
    - (*f*) Steam is passed through a tube containing magnesium powder.
2. Why does stirring increase the rate of solution ?

3. When dilute sulphuric acid is poured on common salt and the mixture is heated, what causes the reaction to go to completion?

4. Complete the following equations, and by reference to the table of solubilities tell which go to completion. (Secs. 144, 145)

$HgNO_3 + KCl$
$CuSO_4 + NaNO_3$
$Na_2CO_3 + HNO_3$
$NaBr + H_3PO_4$
$BaCl_2 + CuSO_4$
$ZnS + H_2SO_4$
$Na_2SO_4 + HCl$
$FeS + H_2SO_4$
$CaCO_3 + HCl$.

5. If steam and iron, inclosed in a glass tube which is sealed at one end and has a tight piston in the other, are heated steadily until they reach equilibrium, in which direction will the equilibrium be displaced, (*a*) by pushing in the piston, (*b*) by forcing more hydrogen into the tube, (*c*) by forcing more steam into the tube?

CHAPTER XV

SULPHUR AND ITS COMPOUNDS

SULPHUR

> "Quickly, O Nurse, bring fire that I may burn
> Sulphur, the cure of ills."
> —Homer's *Odyssey*

147. History.—Sulphur is an element the knowledge of which dates back to antiquity; for even Homer seemed to be aware of the disinfecting qualities of its fumes, as the above quotation would indicate, and the alchemists considered it to be the constituent in bodies that made them inflammable. It was in early times called *brimstone*, meaning "the stone that burns"; and the name is still common.

148. Occurrence.—The fact that sulphurous fumes issue from volcanoes and from crevices in their vicinity is probably responsible for the belief, common among the ignorant, that there is in the interior of the earth burning brimstone. In the crust of the earth there is much sulphur, in both the free and the combined state. The free sulphur is found in almost all volcanic regions, as in Sicily (the most notable deposits in the world), Italy proper, Japan, and Mexico. In Western Louisiana, also, there occurs a great bed of sulphur that has probably been produced by bacteria, and afterwards laid down as a sedimentary deposit. Combined sulphur in the form of sulphides and sulphates is widely distributed. Pyrite, FeS, and sulphides of zinc, lead, and copper form valuable ores; while gypsum, $CaSO_4.2H_2O$, which forms immense deposits in various parts of Canada, is a mineral of great importance.

149. Modifications and properties of sulphur.— (*a*) *Rhombic Sulphur.*—The two forms of this element with which we are most familiar are a powder called flowers of sulphur and a cylindrical stick called roll-sulphur. The latter is yellow, somewhat translucent, and quite brittle. It is almost insoluble in water, slightly soluble in alcohol, but dissolves quite readily in carbon bisulphide. And if a solution in the latter liquid is allowed to evaporate slowly, the sulphur is deposited in transparent, yellow crystals, as beautiful as gems. As these crystals have a rhombic form this variety of sulphur is called *rhombic sulphur.* It has a specific gravity of over 2 and melts at about 114°C. Roll-sulphur is composed entirely, and flowers of sulphur largely, of crystals of rhombic sulphur; but these crystals are much crowded in the roll-sulphur and somewhat incomplete in both.

(*b*) *Monoclinic Sulphur.*—On the other hand, if sulphur is raised just above its melting-point in a beaker and allowed partly to solidify, and if then the liquid part is poured out of the beaker, the whole interior of the beaker is left lined with projecting needle-shaped crystals of sulphur of a form quite different from that of the rhombic crystals. These crystals have, moreover, properties quite different from those of the rhombic form, as the specific gravity is 1.96, and the melting-point is over 119°C. This variety of sulphur is called *monoclinic sulphur.* If monoclinic crystals are kept at ordinary temperatures they lose their transparency and become opaque, and if one of them is broken after this change, it is found to be composed of large numbers of closely packed rhombic crystals. If, on the other hand, a rhombic crystal is heated for some time to a temperature above 97.6°C., but not so high as to melt it, it becomes opaque and is converted into monoclinic crystals. Thus rhombic crystals are stable at all temperatures below 97.6°C.

Below this temperature other forms become rhombic, but above this temperature the monoclinic form is stable, and other forms become monoclinic. Indeed, the relation between these two forms is much the same as that between ice and water; ice is the stable form below 0°C., and water is the stable form above that temperature. Just as ice and water at 0°C. can be kept in contact without one turning into the other, so monoclinic and rhombic sulphur at 97.6°C. remain in contact without one changing into the other; but if the temperature is raised the rhombic becomes monoclinic, and if the temperature is lowered the monoclinic becomes rhombic. For this reason the temperature, 97.6°C., is called the *transition temperature.* Moreover, in another respect, the two forms are related to each other as are ice and water, for just as when 1 gram of ice becomes water, 80 calories of heat are absorbed, so when 32 grams of rhombic sulphur are converted into monoclinic sulphur, over 2 calories of heat are likewise absorbed.

(*c*) *Liquid and Plastic Sulphur.*—When roll-sulphur is carefully melted it forms a straw-coloured liquid, which is quite mobile; but as the temperature of the liquid is raised the colour darkens to brown, then to black and, further, the liquid becomes so viscous that it will scarcely flow. If the temperature is raised still higher, though still remaining dark, it becomes more mobile as the boiling-point is approached. It boils at about 444.5°C. The vapour given off, as it boils, is yellow or orange-yellow, and this, on meeting the cool air, condenses to a solid. But if the boiling sulphur is poured into water, a third modification of sulphur is formed, called *plastic sulphur,* which is brown, soft, quite elastic, and gummy. This, quite unlike both the other varieties, is insoluble in carbon bisulphide. In a few days it becomes converted into rhombic sulphur, the stable form at ordinary temperatures.

The light-yellow and the dark viscous liquid are allotropes of sulphur. They differ not only in colour and viscosity, but each, when suddenly cooled by pouring it into water, is converted into a different product. The dark-coloured variety, as we have just stated, is converted into plastic sulphur, while the yellow variety is at once converted into ordinary rhombic sulphur.

To understand the relationship between plastic and rhombic sulphur it is necessary to compare them with certain conditions of water. If water is cooled under favourable conditions it may fall much below its freezing temperature, 0°C, and still remain quite fluid. It is then said to be *super-cooled*. If into this super-cooled water the smallest particle of ice is dropped, the water begins to freeze at once, and the temperature generally rises to 0°C. Some super-cooled liquids, however, solidify very slowly. Now, plastic sulphur is really the super-cooled, viscous liquid sulphur, and like other super-cooled liquids, it eventually becomes converted entirely into the solid form.

Besides these already mentioned, there are probably five other solid allotropes, but they are not of great importance.

150. Chemical properties.—Sulphur in its chemical properties closely resembles oxygen. With some of the metals, such as mercury and silver, it unites at ordinary temperatures to form the sulphides:

$$2Ag+S \longrightarrow Ag_2S,$$
$$Hg+S \longrightarrow HgS.$$

Again, copper, iron, and zinc, when heated and put into sulphur vapour, glow and are converted into the sulphides. Sulphur also combines with some of the non-metals. For instance, in oxygen it burns to produce sulphur dioxide, SO_2. All oxidizing agents, in the presence of water, convert it into sulphuric acid. Its vapour density at very high temperatures is 64, corresponding to the formula, S_2; but just above the boiling-point its vapour density is about 192, corresponding to the formula, S_6. It is bivalent, quadrivalent, and hexavalent. Its most common hydride is H_2S, and its two most important oxides are SO_2 and SO_3.

151. Extraction.—Up to about 1906 the world's supply of sulphur came largely from Sicily. There it is found mixed intimately with other rock material and is extracted in a primitive manner. For this purpose, large circular excavations are made on the side of a hill (Fig. 44), and are lined with brick (A). In these excavations the lumps of ore (C), are arranged so as to leave ventilation flues (b) passing up among the lumps. The ore is heaped up at the top to form a dome, which is covered with an impervious layer (c). The sulphur at the bottom is ignited and by its combustion it gradually heats all parts of the heap. When the sulphur is melted by the heat it sinks to the sloping bottom (e), and flows along it out through (a) into the chamber (B).

Fig. 44.—Method in use in Sicily of Extracting Sulphur

A. Brickwork on the side of a hill. a. Opening through which sulphur flows out into chamber. (B). b. Ventilating shafts through the sulphur. C. Sulphur ore. c. Powdered sulphur ore.

152. Refinement.—Since sulphur prepared in this way is quite impure, it is refined in a distilling apparatus like that shown in Figure 45. After it has been melted in M it runs into G, where it is vaporized. The vapour passes through D into the large chamber (A), in which it is chilled and condensed into a cloud, which falls to the bottom as flowers of sulphur. When the chamber, however, becomes heated above the melting-point of sulphur, the latter gathers as a liquid (S) on the bottom of the chamber and is run out into slightly conical wooden moulds to form roll-sulphur.

153. Extraction of Louisiana sulphur.—The development of the sulphur beds of Louisiana is one of the triumphs of technology. There great beds of pure sulphur, 150 feet thick, underlie five hundred feet of quicksand, gravel, and porous limestone. Millions of dollars and many lives were spent during fifty years in endeavouring to sink shafts and to mine the sulphur; but the water pressure forced in the shafts, and sulphurous gases suffocated the miners. At last, in 1903, Herman Frasch, an American engineer, solved the problem. He bored a well (Fig. 46) to the bottom of the sulphur bed and placed in it four metal tubes, one within another. Through the two outer tubes (H

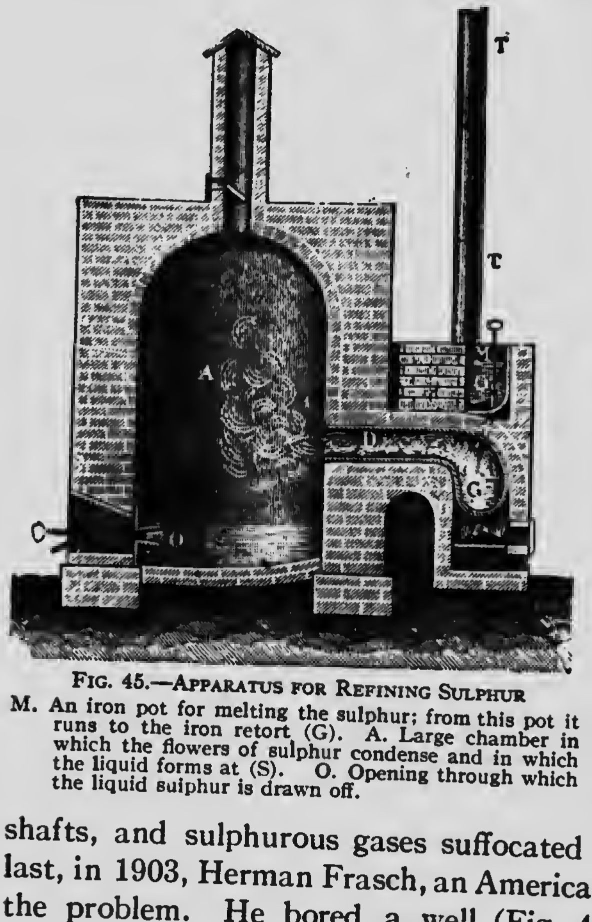


FIG. 45.—APPARATUS FOR REFINING SULPHUR

M. An iron pot for melting the sulphur; from this pot it runs to the iron retort (G). A. Large chamber in which the flowers of sulphur condense and in which the liquid forms at (S). O. Opening through which the liquid sulphur is drawn off.

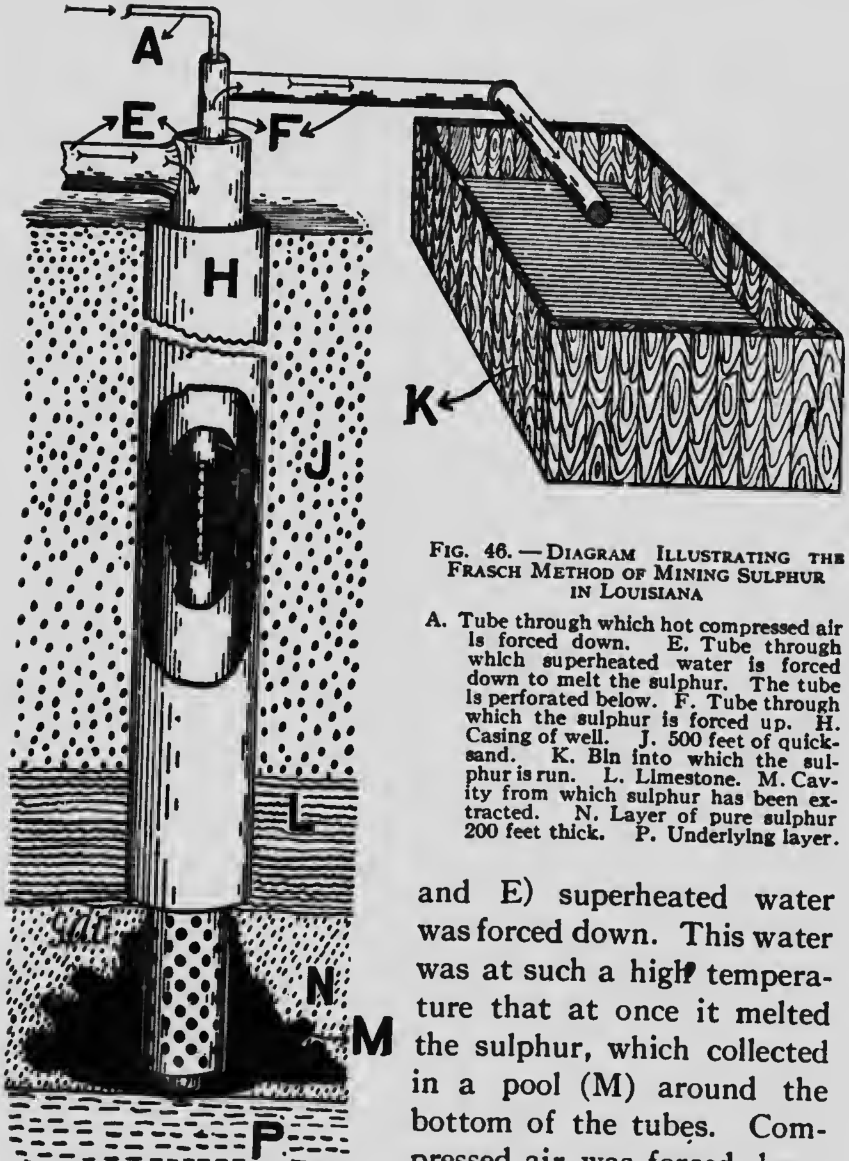


Fig. 46.—Diagram Illustrating the Frasch Method of Mining Sulphur in Louisiana

A. Tube through which hot compressed air is forced down. E. Tube through which superheated water is forced down to melt the sulphur. The tube is perforated below. F. Tube through which the sulphur is forced up. H. Casing of well. J. 500 feet of quicksand. K. Bin into which the sulphur is run. L. Limestone. M. Cavity from which sulphur has been extracted. N. Layer of pure sulphur 200 feet thick. P. Underlying layer.

and E) superheated water was forced down. This water was at such a high temperature that at once it melted the sulphur, which collected in a pool (M) around the bottom of the tubes. Compressed air was forced down through the inner tube (A), and this drove the molten sulphur up in a continual stream through the remaining tube (F). The sulphur on reaching the surface is collected in bins (K) of immense size, one containing as much as 100,000 tons.

Within the last few years the whole sulphur market has been changed; for the Louisiana sulphur companies have wrested from Sicily the position it held for many years as the chief producer of sulphur. and these companies now produce about one half of the world's supply and are capable of producing much larger quantities.

154. Uses of sulphur.—The uses of sulphur are various. Large quantities are required for the production of sulphites, which are used in the manufacture of wood-pulp. Much is used in the great vineyards of Europe to sprinkle on grape-vines to prevent the growth of fungi. Again, some is used for the manufacture of gunpowder, and for the vulcanizing of rubber. Large quantities are also required in bleaching wool and silk. It is now also used to a certain extent as a fertilizer.

HYDROGEN SULPHIDE, H_2S

155. Occurrence.—Hydrogen sulphide was first carefully studied by Scheele in 1777. It is one of the gases issuing from volcanoes, and it is also a component of the natural gas found in western Ontario. Moreover, it is found dissolved in the water of sulphur springs, for it is not sulphur, as is popularly believed, but this gas that gives the characteristic taste and odour to such springs. Besides, it is always one of the gases produced during the decay of organic matter.

156. Preparation.—Hydrogen sulphide is usually prepared by acting on ferrous sulphide with hydrochloric or dilute sulphuric acid. But other sulphides may replace ferrous sulphide in this reaction. It can also be prepared in the laboratory by heating together sulphur and paraffin, since the latter contains much hydrogen, which readily combines with the sulphur. The gas can be collected either over hot water or by the displacement of air.

157. Properties.—Hydrogen sulphide is a colourless gas with a very disagreeable odour, resembling that of rotten eggs. It is a little heavier than air, 1 litre of it at N.T.P. weighing 1.54 grams. One litre of water dissolves over three litres of the gas at room temperature. As the gas can be driven entirely out of its aqueous solution by boiling, it resembles in this respect carbon dioxide (Sec. 122), and acts quite differently from hydrogen chloride (Sec. 102). If a jet is inserted in the end of a delivery tube connected with a flask in which the gas is being generated, the gas can be ignited and will burn with a pale flame, producing water and sulphur dioxide:

$$2H_2S+3O_2 \longrightarrow 2H_2O+2SO_2.$$

Now, if a cool evaporating dish is placed in the flame, sulphur is deposited on its surface. It reacts readily with chlorine, forming sulphur and hydrogen chloride:

$$Cl_2+H_2S \longrightarrow 2HCl+S.$$

And in general it will react with any oxidizer, the products being water and either sulphur or sulphur dioxide. If a solution of the gas is allowed to stand, its hydrogen combines with the oxygen of the air to form water, sulphur being deposited. Indeed, this last reaction is typical of its behaviour, for its hydrogen unites readily with the oxygen of compounds, thus reducing them. For example, if it is passed through sulphuric acid it at once reduces it to sulphur dioxide and water:

$$H_2SO_4+H_2S \longrightarrow 2H_2O+SO_2+S.$$

This action may be viewed as follows: Sulphuric acid is the substance formed by the union of sulphur trioxide and water and its formula may be written $H_2O.SO_3$. Now, the hydrogen of the hydrogen sulphide unites with one third of the oxygen in SO_3 to form water, thus reducing sulphur trioxide to sulphur dioxide:

$$SO_3+H_2S \longrightarrow H_2O+SO_2+S.$$

As hydrogen sulphide when inhaled acts as a poison, it should never be allowed to escape into the laboratory. Indeed, if it composes only $\frac{1}{800}$ of the air it is said it will prove fatal to a dog, and, certainly, much less than this proportion of the gas will produce headache and vomiting in a human being.

158. Acid properties.—A solution of hydrogen sulphide in water is a weak acid, turning blue litmus red. Like other acids, it reacts with many metals, their oxides, and their salts, to form sulphides, all of which are insoluble in water except those of sodium, potassium, calcium, and barium. Consequently, if hydrogen sulphide is passed into solutions of metallic salts, the sulphides are usually precipitated:

$$CuSO_4+H_2S \longrightarrow CuS+H_2SO_4.$$

For example, the sulphides of copper, silver, mercury, lead, arsenic, antimony, and tin can be precipitated in this way. But as the sulphides of iron, zinc, and nickel, though insoluble in water, are soluble in dilute acids, they cannot be precipitated by passing hydrogen sulphide into solutions of their salts, for in such a reaction an acid is always formed:

$$ZnCl_2+H_2S \longrightarrow 2HCl+ZnS.$$

As some of the sulphides have bright colours, their formation gives a ready means of identifying the metal. Antimony sulphide, for example, is bright orange, tin sulphide is brown, lead sulphide is black, and zinc sulphide is white.

159. Test for hydrogen sulphide.—The gas can generally be detected by its odour, but if it is present even in small quantities it will blacken paper previously dipped in a solution of a lead salt.

SULPHUR DIOXIDE, SO_2

160. Preparation.—Sulphur dioxide has been known as long as sulphur itself; for when sulphur is burned sulphur dioxide, well-known by its odour, is formed. Not, however, until Priestley had learned to collect gases over mercury instead of water was this gas prepared pure. It issues in considerable quantities from volcanoes, and is always found in towns and cities where much coal or coal-gas is burned, as they always contain some sulphurous component. It may be prepared in a great many ways, only three of which will be described:

(1) If concentrated sulphuric acid is heated with copper, this gas is generated. The reaction may be considered in two stages; first, the copper acts on the sulphuric acid in the usual way, the metal replacing the hydrogen:

$$Cu+H_2SO_4 \longrightarrow CuSO_4+2H.$$

Then the hydrogen reduces the sulphuric acid. Now if we express the formula of sulphuric acid, $H_2O.SO_3$, the hydrogen can be considered to reduce the SO_3 to SO_2, the other atomic weight of oxygen in each molecular weight of sulphur trioxide being converted into a molecular weight of water:

$$2H+H_2O.SO_3 \longrightarrow 2H_2O+SO_2.$$

It is not to be considered, however, that these steps actually follow each other, for the whole reaction takes place simultaneously, but the method of viewing it as a succession of steps is merely a handy device to enable us to correlate it with other well-known reactions. When either carbon or sulphur replaces copper in the reaction, these elements, like the hydrogen above, reduce the sulphur trioxide to sulphur dioxide according to the following equations:

$$S+2H_2O.SO_3 \longrightarrow 2H_2O+3SO_2,$$
$$C+2H_2O.SO_3 \longrightarrow 2H_2O+2SO_2+CO_2.$$

(2) Probably the best method for laboratory purposes is to decompose sodium bisulphite with sulphuric acid:

$$2NaHSO_3+H_2SO_4 \longrightarrow Na_2SO_4+2SO_2+2H_2O.$$

(3) Vast quantities of sulphur dioxide are prepared for making sulphuric acid by heating iron pyrites, FeS, in a furnace in which an abundant supply of air passes over the pyrites. Such a process is called *roasting*.

161. Properties.—Sulphur dioxide is a colourless gas, which, when inhaled, is very irritating to the throat and bronchial tubes; it is also quite poisonous to vegetation. In Sicily, accordingly, where sulphur is prepared in the fields, the burning of the ore is forbidden during the summer or autumn in order that no damage may be done to the crops. Again, in Northern Ontario, where the nickel ores are roasted and the sulphur dioxide is allowed to escape, the surrounding country has been converted into a desert. As it is more than twice as heavy as air and is very soluble in water, it must be collected by the downward displacement of air. The gas can be readily converted into a liquid, and this liquid, stored in tins or bottles, is used largely for disinfection. Indeed, a tin of the liquid, which is inexpensive, is very useful in the laboratory as a source of the gas.

162. Reducing action.—Though sulphur dioxide will not support combustion, yet when the gas with oxygen is passed over hot platinum the two gases largely unite to form sulphur trioxide, SO_3:

$$2SO_2+O_2 \longrightarrow 2SO_3.$$

This reaction is reversible.

To perform this experiment some fibres of asbestos are dipped into a solution of platinum chloride and then strongly heated. The heat drives off the chlorine, and the platinum is left as a very fine powder adhering to the fibres of asbestos, which is now called *platinized asbestos*. The advantage of the latter over a piece of platinum is that it exposes many times as great a surface of platinum. The platinized asbestos is placed in a combustion tube, which is heated to about 400C., and then a mixture of the gases is passed through the tube. In this reaction the platinum acts as a catalyst, and the sulphur trioxide forms a cloud in a flask connected with the combustion tube.

163. Oxidizing agent.—On the other hand, when sulphur dioxide is mixed with hydrogen sulphide the former acts as an oxidizer, converting the hydrogen of hydrogen sulphide into water, the sulphur being deposited The following equation represents the reaction:

$$2H_2S+SO_2 \longrightarrow 2H_2O+3S.$$

164. Acid properties.—When sulphur dioxide is dissolved in water the solution is an acid turning litmus red, generating hydrogen when such a metal as magnesium is added to it, and producing salts when neutralized by bases. As the formula of the salt produced with sodium hydroxide is Na_2SO_3, and the other salts have similar formulæ, we write the formula of the acid H_2SO_3, to suggest the connection between the acid and the salt, and we write the equation for the reaction when sulphur dioxide is passed into water

$$SO_2+H_2O \longrightarrow H_2SO_3.$$

Hence sulphur dioxide is an anhydride (Sec. 178), and because it unites with water to form *sulphurous acid*, it is called *sulphurous anhydride.* A substance, however, with a formula, H_2SO_3, has never been obtained, as the solution yields on evaporation only water and sulphur dioxide.

165. Reducing properties of sulphurous acid.—If a solution of sulphurous acid is left exposed to the air, the oxygen of the air unites with it to form sulphuric acid:

$$2H_2SO_3+O_2 \longrightarrow 2H_2SO_4.$$

Besides, the acid withdraws oxygen from some of its compounds, reducing the compound and itself becoming ulphuric acid. If it is mixed, for example, with a dilute solution of potassium permanganate, a strong oxidizing agent, the sulphurous acid unites with a part of the oxygen to form sulphuric acid, the permanganate being reduced to a colourless compound.

166. Bleaching by sulphur dioxide and sulphurous acid.—When coloured flowers are placed in a vessel of sulphur dioxide, the colour soon disappears, and it is thought in such bleaching that the sulphur dioxide unites directly with the colouring matter. The bleaching, however, is not always permanent, as, when the bleached object is exposed to the air, the colour frequently returns. Sulphurous acid is used commercially to a large extent for bleaching woollen goods, straw, sponges, and silk, which would be injured by chlorine. In the process of bleaching the articles are damped and placed in a room in which sulphur is kept burning for eight hours or more. The sulphurous acid withdraws the oxygen from the colouring matter, and the substance becomes colourless. However, the colourless substance frequently regains in time its original colour. When straw hats, for example, turn brown and sponges turn yellow, it is simply a return to the state in which they were before being bleached. For this and other reasons, sulphurous acid is now being largely replaced as a bleacher by hydrogen peroxide.

167. Other uses of sulphur dioxide and sulphites.—By far the greatest quantity of sulphur dioxide is used for manufacturing sulphuric acid. But it is also used to decolourize syrup, to preserve meat, and to fumigate sickrooms. The sulphites are used for converting wood into pulp.

168. The sulphites.—Sulphites are formed by acting on bases with sulphurous acid. Except those of sodium and potassium they are only slightly soluble in water. A solution of a sulphite gives a white precipitate with barium chloride:

$$K_2SO_3+BaCl_2 \longrightarrow BaSO_3+2KCl.$$

But on the addition of hydrochloric acid the precipitate disappears. This latter reaction distinguishes sulphites from sulphates, for barium sulphate is insoluble in acids. Sulphites can also be detected by the fact that they give off sulphur dioxide when heated with sulphuric acid.

169. Sulphur trioxide.—The method by which this oxide is formed has been already described (Sec. 162). It is usually a clear liquid which dissolves in water to form sulphuric acid:

$$SO_3+H_2O \longrightarrow H_2SO_4.$$

For this reason it is called *sulphuric anhydride.*

SULPHURIC ACID, H_2SO_4

"Sulphuric acid is without doubt the most important and useful acid known, as by its means nearly all other acids are prepared, whilst its manufacture constitutes one of the most important branches of modern industry, owing to the great variety of purposes for which it is needed, as there is scarcely an art or trade in which in some form or other it is not employed."

—*Sir Henry Enfield Roscoe*

170. History.—The first to prepare this most important of all chemicals was an old monk of the fifteenth century, who obtained it by heating green vitriol, $FeSO_4.7H_2O$. For several centuries it was prepared in this way and was called *oil of vitriol.* About 1740, Ward, a quack doctor, first introduced the modern method into England. Having placed some water in the bottom of an immense glass bottle, he then suspended a red-hot ladle inside the bottle and placed in it sulphur and nitric acid. The sulphur was oxidized to sulphur trioxide by the nitric acid, and this oxide dissolved in the water to form sulphuric acid. Charge after charge was placed in the ladle and the successive quantities of sulphur trioxide thus formed dissolved in the water. By this new method he was able to reduce the price of the acid from six dollars to fifty cents a pound. Lead chambers soon replaced the more fragile glass bottles, and the price rapidly dropped until to-day it costs less than one cent a pound. Probably eight million tons are produced annually.

171. Properties of the acid.—Sulphuric acid, as it is sold in the market, is a syrupy liquid almost twice as heavy as water. In this form it contains some water; in fact a pure substance answering to the exact formula, H_2SO_4, is seldom seen, though it can be prepared. When water is added to concentrated sulphuric acid, so much heat is produced that it is possible by this means to raise the temperature high enough to produce steam. However, it is always safer to add the acid—a little at a time—to the water, as in this way the heat is generated more slowly and has a large mass of water to warm. It can readily be solidified by cooling. Its high boiling-point, 338°C., has much to do with its great value, as on account of this property it is able to expel acids with a lower boiling-point from their salts. (Sec. 145)

172. Dehydrating action.—As sulphur trioxide is enormously soluble in water, a few drops of the latter dissolving a large bottle of the solid, we can be quite certain that strong sulphuric acid will be a good drying or dehydrating agent (Sec. 63). Indeed, if a bottle of the acid were left open, the acid would absorb water from the air until finally the liquid would overflow the bottle. It is thus one of the very best drying agents used in the laboratory. It not only absorbs water from the air, but also many substances containing hydrogen and oxygen as constituents are decomposed by it, the hydrogen and oxygen being withdrawn in the proportion in which they are present in water. Sugar, for example, has a formula $C_{12}H_{22}O_{11}$, and when acted on by sulphuric acid only a black mass of carbon is left, the hydrogen and oxygen being completely removed as water. For the same reason the acid chars wood, paper, straw, etc. In the same way it produces severe wounds when it comes in contact with the skin. These wounds are sometimes produced by spiteful people "throwing vitriol".

173. Action on metals.—We have already studied the action of the concentrated acid on copper (Sec. 160). The concentrated acid acts in a similar manner when heated with mercury, silver, lead, and tin, generating sulphur dioxide. When dilute, however, it liberates hydrogen when acted on by zinc, magnesium, or iron, as has already been observed in studying that gas (Sec. 46). On the other hand, gold and platinum are not attacked either by the dilute or the concentrated acid. As lead is attacked by the acid only when a high concentration is reached, it is used to line the vessels in which the acid is manufactured, and platinum or glass is necessary only for the final concentration.

174. Test for sulphuric acid.—When barium chloride solution is added either to sulphuric acid or to a solution of one of its salts, a white precipitate of barium sulphate is produced, which is insoluble in any of the common acids. This serves as a distinguishing test for sulphuric acid.

175. Uses of sulphuric acid.—There is scarcely a product that we use that has not required sulphuric acid in some stage of its preparation. The glass in the vessels we use at the table had, as a component in its preparation, soda, which in turn was made by means of sulphuric acid. The cereals and vegetables we eat were grown on soil made productive by superphosphates and ammonium sulphate, both prepared by means of this acid. The baking-powder used to make pastry light is composed of baking-soda and, possibly alum, which have both required this acid for their preparation. The match that kindles the fire contains phosphorus produced by the same acid. Our clothing has met the products of this acid at every turn. Cottons and linens are bleached by means of chloride of lime, and the chlorine that enters into the composition of this bleaching agent is derived from common salt, which is started on its course toward chlorine by the addition of sulphuric acid. The dyes which are manufactured from coal-tar products by the help of this acid, are made to adhere to the cloth by the use of mordant salts, which again are prepared by means of the same chemical. Gun-cotton, nitro-glycerine, dynamite, and cordite, the great explosives used in war, are all products of nitric acid, which itself is prepared by means of sulphuric acid. The hydrogen that fills air-ships, the many appliances dependent on the storage-cell, all owe their production to the same acid. In fact, one would not be far astray in stating that the industries of a country can be measured by the amount of sulphuric acid it uses. In the laboratory we have used it as (1) a drying agent (Sec. 102); (2) an oxidizing agent (Sec. 157); (3) an acid (Sec. 156); (4) a dehydrating agent and acid (Sec. 125); (5) and as an oxidizing agent and acid (Sec. 160).

176. Manufacture of sulphuric acid.—We have already learned (Sec. 162) that, in the presence of a catalyst, sulphur dioxide and oxygen unite to form sulphur trioxide, and that it is only necessary to dissolve the higher oxide in water to produce sulphuric acid:

$$2SO_2 + O_2 \longrightarrow 2SO_3,$$
$$SO_3 + H_2O \longrightarrow H_2SO_4.$$

These reactions form the basis of the methods by which all the sulphuric acid of commerce is produced. There are two catalysts used at the present time and the methods according to the catalyst used are called (1) *the lead chamber method* and (2) *the contact method.*

(1) *The lead chamber method.*—The method of preparation introduced into England by Ward (Sec. 170), developed into the lead chamber method, which is still almost exclusively used there. Figure 47 shows the appearance of a sulphuric acid factory. In the pyrite ovens, (B), iron pyrites is roasted producing sulphur dioxide, which with air and nitrogen peroxide, N_2O_4, pass up through the Glover tower (G). This tower is filled with stones down which dilute sulphuric acid trickles. This sulphuric acid, which contains nitrogen peroxide dissolved

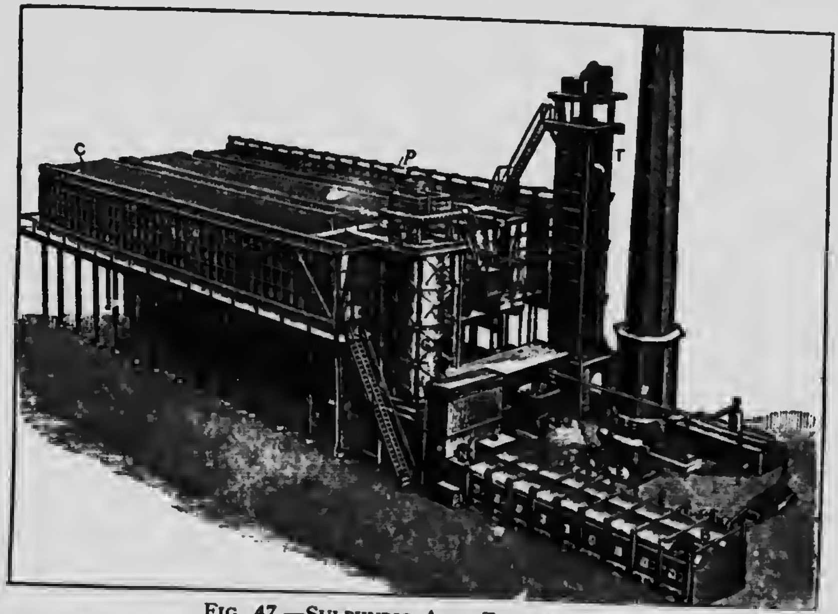


Fig. 47.—Sulphuric Acid Factory
B. Pyrite burners in which sulphur dioxide is formed. N. Nitre pots where oxides of nitrogen are produced. G. Glover tower. C. Leaden chamber. P. Pipe conveying the gases from the lead chamber to Gay-Lussac tower. T. Gay-Lussac tower.

in it, comes from the Gay-Lussac tower, (T), which will later be described, and before passing down the Glover tower is diluted with water. The hot gases passing up through the Glover tower withdraw the peroxide and part of the water from the acid. The mixture of gases then passes through several lead chambers (C) into which steam is also being injected. Here the nitrogen peroxide acts as a catalyst, causing the sulphur dioxide to combine with the oxygen of the air to form sulphur trioxide, which immediately combines with the steam to form sulphuric acid. The acid rains down on the bottom of the lead chambers. The lead chambers of the factory are of immense size, one being large enough to enable 250 people to sit down to a banquet together. The nitrogen peroxide, which is not destroyed during the operation, and the nitrogen of the air pass out through the pipe (P) into the Gay-Lussac tower. The purpose of this tower is to prevent the escape and loss of the nitrogen peroxide. To accomplish this, strong sulphuric acid trickles down through the tower over stones and dissolves the nitrogen peroxide from the ascending gases, so that only the useless nitrogen escapes. This acid from the Gay-Lussac tower is then pumped over to the Glover tower where the nitrogen peroxide is withdrawn from it again as already described. As lead is not attacked by sulphuric acid, the towers and chambers are constructed of this metal, which is supported and strengthened externally by wooden supports.

(2) *Contact Method.*—Until quite recently all sulphuric acid was manufactured by the method just described; but now a commercial method of using platinum as a catalyst has been discovered, and this new method, called the contact process, is rapidly ousting the older one. The difficult part of this process is to obtain the sulphur

dioxide and oxygen perfectly pure before passing them over the platinum; if not pure they "poison" the platinum so that it will not act catalytically. The sulphur trioxide formed is passed into a solution of sulphuric acid, where the oxide unites with the water to produce more acid. At Sulphide in Eastern Ontario, where pyrite is abundant for making sulphur dioxide, a large factory for manufacturing the acid by this method is located.

177. Sulphates.—The sulphates are prepared by acting with sulphuric acid on the metals, metallic oxides, hydroxides, and carbonates; also by heating metallic chlorides and nitrates with sulphuric acid. All the sulphates are quite soluble, except those of lead, calcium, and strontium, which are slightly soluble, and barium sulphate, which is insoluble. The same test is used for soluble sulphates as for sulphuric acid.

QUESTIONS

1. Why does silver tarnish rapidly in rooms where coal-gas is burned? (Sec. 158)

2. Why do paints containing white lead rapidly turn dark in factory towns? (Sec. 158)

3. Describe how sulphur can be obtained from hydrogen sulphide. (Sec. 157)

4. Why is sodium sulphate not used for preparing sulphuric acid, as sodium chloride is used for preparing hydrochloric acid?

5. Sulphur dioxide and sulphurous acid are said to be reducing agents. Explain the statement and give examples of their use as reducers. (Secs. 162, 165)

6. What impurities would you expect to find in sulphuric acid manufactured in the lead chambers?

7. Describe the changes that occur when roll-sulphur is heated from ordinary temperatures to its boiling-point.

8. Mention reactions in which hydrogen sulphide acts as a reducing agent. Write the equations.

9. A solid is known to be a sulphide, a sulphite, or a sulphate. How would you find out which it is? (Secs. 159, 168)

10. How can sulphur dioxide be distinguished from hydrogen chloride, hydrogen sulphide from hydrogen, and carbon dioxide from sulphur dioxide? State as many ways as possible.

11. How can traces of hydrogen sulphide be removed from sulphur dioxide? (Sec. 157)

12. Describe the processes that a piece of native sulphur undergoes before it is put on the market as flowers of sulphur. (Secs. 152, 153)

13. If concentrated sulphuric acid is poured into water, why should it be poured slowly? (Sec. 171)

14. A dish containing sulphuric acid is usually placed in the case of a delicate balance; also in a clock that keeps exact time. Explain why. (Sec. 172)

15. The industrial development of a country is said to be indicated by the amount of sulphuric acid used. Explain this statement. (Sec. 175)

16. Why will a rubber band stretched over a silver coin blacken it? (Secs. 154, 150)

17. Why are egg-spoons usually plated with gold rather than with silver?

18. When a chimney takes fire, the fire is frequently extinguished by burning a shovelful of sulphur at the opening near the bottom of the chimney. Why is this done?

19. In sulphur springs is it sulphur that is dissolved in the water? Give a reason for your answer. (Sec. 155)

20. What allotropic form of sulphur occurs in roll-sulphur and in flowers of sulphur?

21. Starting with iron filings, sulphur, and hydrochloric acid, give directions for making hydrogen sulphide.

22. How can hydrogen sulphide be used to distinguish a zinc salt from a lead salt, an antimony salt from a lead salt? (Sec. 158)

23. What advantages has sulphur dioxide as a bleacher? What advantages has chlorine? Compare the nature of the chemical action when each bleaches. (Secs. 111, 166)

24. If a bottle of sulphuric acid is left unstopped it increases in weight. Explain.

25. A silver coin weighs 2.48 grams and is ten per cent. copper. Calculate how many grams of copper sulphate and of silver sulphate can be made by converting the metals into their sulphates.

26. How many pounds of sulphuric acid can be produced from 100 pounds of sulphur?

27. An oxide of sulphur contains 50 per cent. sulphur. Its density is 32 (H. = 1). What is its formula? (Sec. 76)

28. The density of sulphur vapour from 860°C. to 1040°C. is 2.23 (air = 1). If its atomic weight is 32 what is its formula between these temperatures. (Sec. 76)

29. What volume of oxygen measured at 20°C. and 750 mm. pressure is required to produce, (*a*) 1000 litres of sulphur dioxide at the same temperature and pressure, (*b*) 1000 grams of sulphur trioxide?

CHAPTER XVI

OXIDES, ACIDS, BASES, SALTS

178. Oxides.—Oxides are formed by the union of oxygen with another element. A substance, however, that contains oxygen and two or more other elements is not generally called an oxide, but is given some other name. HgO, for example, is called mercury oxide, but $HgNO_3$ is called mercurous nitrate. It has been already observed that many oxides, such as those of mercury, tin, lead, and sulphur, are formed by the heating of the elements in air, but some cannot be formed in this way. Oxides may be divided into several classes according to the nature of their chemical action.

(*a*) *Acidic oxides or anhydrides.* These combine with water to form acids. Sulphur trioxide, SO_3, and phosphoric oxide, P_2O_5, are examples of this class, as they combine with water to form sulphuric acid and phosphoric acid:

$$SO_3+H_2O \longrightarrow H_2SO_4,$$
$$P_2O_5+3H_2O \longrightarrow 2H_3PO_4.$$

The great majority of these oxides are formed by oxygen combining with a *non-metal.*

(*b*) *Basic oxides* are those which combine with water to form bases. An example is calcium oxide, CaO, which combines with water to form calcium hydroxide, $Ca(OH_2)$. The oxide, however, as well as the acid, is by some chemists called a base. Basic oxides also combine directly with acids to form salts and water:

$$ZnO+H_2SO_4 \longrightarrow ZnSO_4+H_2O.$$

The basic oxides, which are generally formed by oxygen combining with a *metal* are, with the exception of those of sodium and potassium, much less soluble in water than the anhydrides.

(*c*) *Peroxides* are oxides that have a greater proportion of oxygen combined with the metal than has the basic oxide: for example, Na_2O is the basic oxide of sodium, Na_2O_2 is sodium peroxide; BaO is the basic oxide of barium, but BaO_2 is the peroxide. This character alone, however, is not enough to distinguish peroxides. When they react with acids, they produce either hydrogen peroxide, H_2O_2, or water and oxygen:

$$BaO_2+H_2SO_4 \longrightarrow BaSO_4+H_2O_2,$$
$$2MnO_2+2H_2SO_4 \longrightarrow 2MnSO_4+2H_2O+O_2;$$

and when they are heated oxygen is generally produced. Hence, as they give up part of their oxygen readily they are usually strong oxidizing agents.

(*d*) *Indifferent or miscellaneous oxides.* This is simply a class in which to place those oxides that do not belong to any of the other three classes.

179. Acids.—

> "The history of the development of the terms acid, base, and salt furnishes examples of the tyranny of phrases. Scheele called the new gas (chlorine) he discovered *dephlogisticated marine acid*, and for many years every one who examined this gas assumed it to be an acid. Lavoisier . . . in the word oxygen perpetuated his view that this element is *the* acid producer. The labours of a vast number of chemists during more than half a century were required to prove that Lavoisier had drawn a boundary-line which does not exist."
>
> —*Pattison Muir*

The word acid is derived from a Latin word *acidus*, meaning sour. Vinegar was the acid best known to the ancients. The alchemists were much interested in acids, on account of their great power of dissolving substances, as they believed that the baser metals must be dissolved before they could be converted into gold. Lavoisier thought that all acids contain oxygen, and it was for this reason that he gave oxygen its name, which is derived from the Greek word, *oxys*, acid, and the root, *gen*, to generate, and for many years this idea held the field, although many facts had been investigated showing that several acids did not contain this element. Finally Sir Humphry Davy propounded the *hydrogen theory* of acids, which scientific investigation has supported so completely that the fact that all acids contain hydrogen, has now become one of the best established facts of chemistry.

Acids are formed by dissolving in water various substances such as hydrogen chloride, HCl; sulphur dioxide, SO_2; sulphur trioxide, SO_3; phosphorus pentoxide, P_2O_5; carbon dioxide, CO_2; or hydrogen sulphide, H_2S. In some cases pure substances in which the oxide has combined with water can be obtained from the solution. For instance, when phosphorus pentoxide, P_2O_5, is dissolved in water, a compound may be obtained with the composition $P_2O_5.3H_2O$ ($=2H_3PO_4$). Similarly, on freezing sulphur trioxide solution, a compound of the formula $SO_2.H_2O$ ($=H_2SO_4$) crystallizes out. Such solutions are generally said to contain the acids H_3PO_4 and H_2SO_4 respectively.

On the other hand, from solutions of carbon dioxide, sulphur dioxide, and many other acids, compounds of the anhydride with water have never been isolated, but on account of the analogy with such oxides as sulphur trioxide and phosphorus pentoxide, it is customary to say that these solutions contain the acids H_2CO_3,

($=CO_2.H_2O$), H_2SO_3, ($=SO_2.H_2O$), etc. Moreover, these formulæ have the advantage of being analogous to the formulæ of many of the commoner salts which the acids form, and which, being pure substances, have definite formulæ ascertainable by analysis. For example:

H_2SO_3	Hydrogen sulphite or sulphurous acid,
Na_2SO_3	Sodium sulphite,
K_2SO_3	Potassium sulphite.

The following are some of the most evident properties of aqueous solutions of acids:

(*a*) They taste sour, turn blue litmus red, make pink phenolphthalein colourless, and change the colour of other organic dyes.

(*b*) They react with zinc and, while they usually liberate hydrogen, in some cases the hydrogen is not liberated, but reacts further with the acid.

(*c*) Their hydrogen can be replaced by the various metals to form salts.

(*d*) They conduct electricity.

(*e*) They react on sodium or calcium carbonate with effervescence.

While some acids lack some of these properties, and it may occasionally be difficult to decide whether a substance is an acid or not, the acids studied in an elementary course have most of these characteristics well defined, and no difficulty will be experienced in identifying their acid character.

Hydrogen chloride, nitric acid, and probably all other acids, if obtained quite free from water show none of these acid properties. As a result of this fact having been only recently discovered, a little confusion has arisen as to whether the substances or the aqueous solutions should be called the acids, and up to the present the term is used for both. The most important characteristic of these substances, from the chemical standpoint, is their ability to form salts by having their hydrogen replaced by metals. From sulphuric acid, H_2SO_4, is formed a whole series of salts such as Na_2SO_4, K_2SO_4, $ZnSO_4$, $Al_2(SO_4)_3$, and all other acids form similar series.

Many common domestic substances contain acids. For example, vinegar, green fruit, lemons, grape-fruit, lime-juice, sour milk, canned tomatoes, taste sour. Many plants such as the buttercup, shamrock, oxalis, contain acids. It is well known, too, that from ants can be obtained a pungent acid, called formic acid (from the Latin *formica*, an ant).

180. Bases.—Ashes were used from the earliest times for their cleansing properties, and substances that, like them, were caustic and dissolved grease, were called *alkalies*, a name derived from an Arabic word, meaning the ashes of a plant. It was early observed that substances of this kind when mixed with acids destroyed the acid properties of the latter.

The oxides of the metals frequently unite with water to form bases, as was stated in Section 178. Solutions of bases in water have the following characteristics:

(*a*) They feel smooth to the touch, have a characteristic taste, turn red litmus blue, colourless phenolphthalein pink, and change the colour of many other organic dyes.

(*b*) They neutralize acids to form salts and water in the manner shown in the following equation:

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O.$$

It will be noticed that the metal of the base and the hydrogen of the acid change places.

(*c*) They conduct electricity.

(*d*) They are all solutions of hydroxides, having formulæ of the form $M(OH)$, $M(OH)_2$, $M(OH)_3$, where M is the symbol for a metal.

While the bases of sodium, potassium, and ammonium are very soluble in water, the bases of the other metals are either slightly soluble, or quite insoluble. The soluble bases are called alkalies.

181. Salts.—Salts have already been defined in describing acids, as they are the substances formed from acids by replacing the hydrogen with metal. Like acids and bases their solutions conduct electricity.

When an acid and a base are mixed in such a proportion that a solution is obtained which contains a salt and has none of the characteristics of either an acid or a base, the operation is called *neutralization*.

182. Formation of salts.—One of the operations most frequently performed, whether in scientific research or in chemical industries, is the preparation of a salt. Frequently during such an operation there is a second substance formed; accordingly, the substances chosen to react must be of such a character that the salt can be readily separated from this other substance. The methods of preparing insoluble and soluble salts in solution are usually different, and will be considered first.

(*a*) *Formation of soluble salts in solution.* The corresponding acid acts on (1) a metal, (2) an oxide, (3) an hydroxide, or (4) a salt of a volatile acid.

$$(1)\quad H_2SO_4+Zn \longrightarrow ZnSO_4+H_2.$$

The hydrogen formed escapes and leaves only the salt, zinc sulphate, in solution.

$$(2)\quad H_2SO_4+Na_2O \longrightarrow Na_2SO_4+H_2O.$$

$$(3)\quad H_2SO_4+2NaOH \longrightarrow Na_2SO_4+2H_2O.$$

As in both of these cases water is the other product, the required salt is the only substance in solution and can be readily obtained by evaporation.

$$(4)\quad H_2SO_4+Na_2CO_3 \longrightarrow Na_2SO_4+H_2O+CO_2$$

$$H_2SO_4+FeS \longrightarrow FeSO_4+H_2S.$$

Since H_2S and CO_2 are both gases they at once escape and leave the salt alone in solution. It would not do to react on sodium phosphate with sulphuric acid,

$$3H_2SO_4+2Na_3PO_4 \rightarrow 3Na_2SO_4+2H_3PO_4,$$

for a mixture of sodium sulphate and phosphoric acid would be present in the solution; and, as phosphoric acid is not volatile, it is very difficult to separate it from the salt. Accordingly, only salts of volatile acids, or salts of acids which quickly decompose into volatile substances, can be used.

(*b*) *Formation of insoluble salts in solution.* — For the reaction there should be selected two soluble salts that will produce the required insoluble salt and a soluble salt. Suppose silver chloride is required, then a silver salt and a chloride are chosen, so that the second salt formed will be soluble:

$$AgNO_3+NaCl \rightarrow AgCl+NaNO_3.$$

As silver chloride, $AgCl$, is insoluble and sodium nitrate, $NaNO_3$, is soluble, the required salt, silver chloride, can be separated by filtration. However, the method of preparing silver chloride represented in the equation,

$$Ag_2SO_4+BaCl_2 \rightarrow BaSO_4+2AgCl,$$

would not be practicable, as the barium sulphate, $BaSO_4$, as well as the silver chloride, is insoluble, and it would be impossible to separate the two salts formed.

(*c*) *Combination of elements:*

$$2Na+Cl_2 \rightarrow 2NaCl.$$

$$S+Fe \rightarrow FeS.$$

(*d*) *Combination of an anhydride and basic oxide:*

$$CO_2+CaO \rightarrow CaCO_3.$$

QUESTIONS

1. Write equations showing the formation of sodium chloride, NaCl, in as many ways as you can. Use only methods in which it can be readily separated from any other substance formed at the same time (Sec. 182).

2. What is meant by a volatile acid? Name several.

3. How can you prepare an insoluble salt?

4. What acid and what base yield sodium chloride when they neutralize each other?

5. If an acid is spilled on clothing, what kind of substance should be applied to stop its action?

6. When a corrosive acid is swallowed, what antidote should be taken?

7. Lime-water is taken by a person who is suffering from acidity of the stomach. Explain the action.

8. When canned tomatoes taste too sour, a little soda ($NaHCO_3$) is frequently added, and a frothing is at once observed. Explain the purpose of adding the soda and the cause of the frothing. Try the experiment.

9. What weight of sulphuric acid is required to neutralize 20 grams of sodium hydroxide?

10. After neutralizing a solution of sodium hydroxide with nitric acid, and evaporating the solution, there remain 100 grams of sodium nitrate. What weight of each substance is used?

11. A solution containing 30 grams of hydrogen chloride in 100 grams of water is mixed with a solution containing 30 grams of sodium hydroxide in 100 grams of water, and the whole is boiled dry. What substance is left and what substances boil off? How much of each?

CHAPTER XVII

THE COMPOUNDS OF NITROGEN

183. Chili saltpetre.—In the northern part of Chili lies a peculiar geological formation in one of the most dreary and desolate desert wastes of the world. It extends in a strip about 2 miles wide for 260 miles, and from this ribbon of desert comes the greater part of the world's supply of nitrates. Figure 48 shows a diagrammatic section through the salt bed Under a loose layer of sand and pebbles (A) 2 or 3 inches thick lies a layer of the same materials (E), cemented together by salt and Chili saltpetre. Below this is a white stratum (F) from 1 to 5 feet thick called "caliche" (kā-lē′-che). The caliche contains a large quantity of Chili saltpetre, which is dissolved, filtered, recrystallized, and packed in bags to be shipped over sea. The origin of these saltpetre beds is rather uncertain, but their presence in Chili is possible only because the region is rainless. The saltpetre

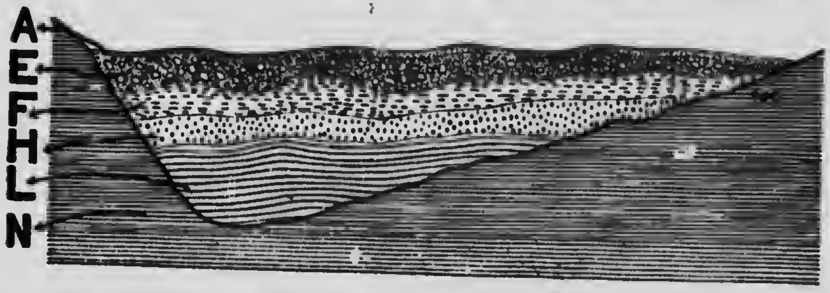


FIG. 48.—CHILI SALTPETRE BEDS
A. Loose layer of sand and pebbles. E. Layer of sand and pebbles cemented together, with salt and Chili saltpetre. F. Caliche layer. H. Layer of sodium chloride, etc. L. Layer of clay and loam. N. Bed rock.

mines are owned almost entirely by British capitalists, and over 2,500,000 tons, valued at $50,000,000, are exported annually. While the salt is used in considerable quantities for manufacturing nitric acid and ordinary saltpetre, the larger part is used as a fertilizer. Chili saltpetre is also called cubic saltpetre, and its chemical name is sodium nitrate, $NaNO_3$.

184. Ordinary saltpetre, nitre, or potassium nitrate has been known from very early times. Where there is much organic matter in the soil, as in cattle yards, or near Eastern cities which have no sanitary arrangements, ammonia and ammonium compounds are formed, which are converted by bacteria into ordinary saltpetre. In these conditions, it gradually forms as a white incrustation on the surface of the soil. This incrustation is dissolved out by water and is recrystallized. In this manner, considerable quantities of saltpetre are produced in India and Persia, but at the present day by far the largest quantity is made by the action between solutions of sodium nitrate and potassium chloride:

$$NaNO_3+KCl \longrightarrow KNO_3+NaCl.$$

The sodium chloride and potassium nitrate are separated from the solution by taking advantage of their different solubilities. Ordinary saltpetre is used in making gunpowder and for preserving meat.

185. Properties of the saltpetres.—Both the saltpetres are very soluble in water, and on evaporation of the water the crystals formed by the two are different. Sodium nitrate is deliquescent while potassium nitrate is not. When they are heated they both melt, and at a higher temperature decompose into oxygen and the nitrite:

$$2NaNO_3 \longrightarrow 2NaNO_2+O_2.$$

NITRIC ACID, HNO_3

186. History.—This acid has been long known, and was early called *aqua fortis*, which means "strong water". This name was given on account of its property of dissolving silver and all the other metals except gold and platinum. It was first prepared in the modern way by Glauber; while that careful English experimenter, Cavendish, prepared it from the air by a method that is just now beginning to be used commercially (Sec. 195). Cavendish, moreover, was the first to determine its composition.

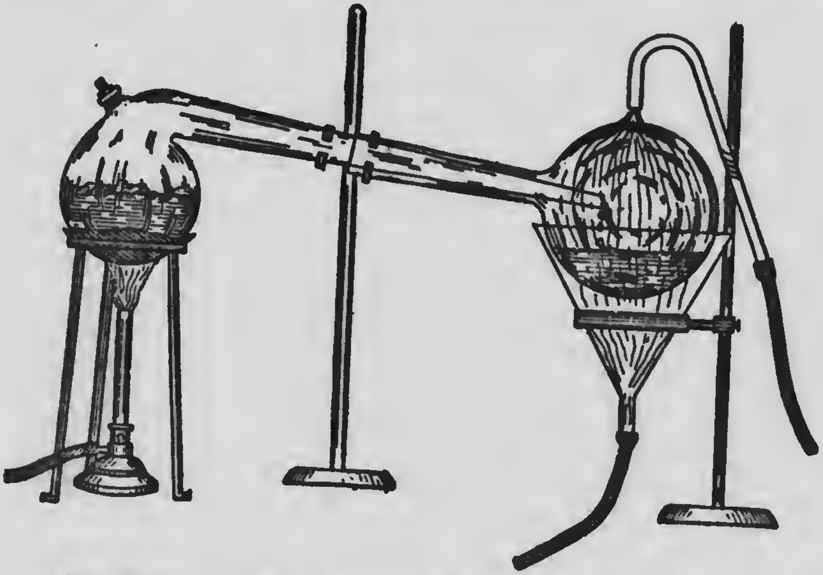


Fig. 49.—Apparatus for Making Nitric Acid in the Laboratory

187. Preparation.—In the laboratory nitric acid is prepared by first mixing in a glass retort (Fig. 49) equal parts of sodium nitrate and concentrated sulphuric acid, and then heating the retort gently; the nitric acid, being volatile at low temperatures, is distilled over and condenses in a flask immersed in cold water. The usual reaction is expressed by the following equation:

$$NaNO_3+H_2SO_4\rightarrow NaHSO_4+HNO_3.$$

If the retort, however, is heated more strongly, a further reaction takes place, expressed by the following equation:

$$NaNO_3+NaHSO_4\rightarrow Na_2SO_4+HNO_3.$$

But since the increased heat necessary to produce this latter reaction decomposes part of the nitric acid, usually only the first reaction is employed both in the laboratory and in manufacturing establishments. Commercially nitric acid is prepared from the same two substances as are used in the laboratory method. The mixture of sodium nitrate and sulphuric acid is charged into a retort (Fig. 50, A) made of cast iron, and as the retort is heated the nitric acid is driven over and condenses in a series of earthenware vessels, (B). Other methods of manufacturing it from the air are described in Section 195.

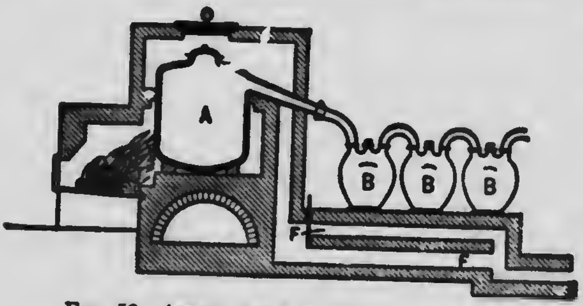


FIG. 50—APPARATUS FOR MANUFACTURING NITRIC ACID
A. Cast iron retort above which is an opening for charging it. B. Glass vessels in which the acid condenses.

188. Properties.—The pure substance, HNO_3, has no action on metals or limestone. Generally, however, it is used diluted with water. Such a solution of the acid has a slight smell and acts vigorously on all metals except gold and platinum; but, unlike other acids, no hydrogen is produced when it acts on a metal, except in the case of magnesium. In fact, the action on metals varies a good deal according to the conditions, a concentrated acid acting differently from one more dilute. This peculiar action of nitric acid with metals depends largely on the fact that it is a very powerful oxidizer, and the hydrogen replaced by a metal may be considered to be oxidized to water by the acid, which is, of course, reduced during the reaction. Considering two molecular weights of nitric acid to be $H_2O.N_2O_5$, the nitric anhydride, N_2O_5, may be reduced by the hydrogen through any of the following stages:

$$N_2O_5 \rightarrow N_2O_4 \rightarrow N_2O_3 \rightarrow 2NO \rightarrow N_2O \rightarrow N_2 \rightarrow 2NH_3.$$

And any of these substances may appear as one of the final products, depending on how far the reduction of the nitric acid goes. For example, with dilute acid zinc gives nitrous oxide, N_2O, copper gives nitric oxide, NO; with more concentrated acid zinc produces ammonia, NH_3, while copper liberates nitrogen peroxide, N_2O_4. Thus we see it is quite impossible to express by an equation what the reaction may be when nitric acid and a metal react, for the reaction may vary a great deal during the progress of a single reaction, since the strength of the acid is continually decreasing.

Nitric acid, as has been stated, is a powerful oxidizing agent; accordingly, it reacts on some non-metals, converting them into their highest oxidation product. Sulphur, for instance, is converted into sulphur trioxide, SO_3, and phosphorus into phosphoric oxide, P_2O_5. Hence when fuming nitric acid acts on sulphur or phosphorus, sulphuric or phosphoric acid is formed, the oxides uniting with the water present.

The decomposition of nitric acid by strong heat can be demonstrated as follows: A long-stemmed clay pipe is held obliquely with the end of its stem placed under the mouth of a bottle of water inverted in a vessel of water. The stem is heated until it is red and then a few drops of nitric acid are poured into the bowl. As the acid flows through the hot part of the stem it is decomposed and oxygen collects in the bottle:

$$4HNO_3 \longrightarrow 4NO_2+2H_2O+O_2.$$

189. Nitrates.—The nitrates crystallize well and are all soluble in water. They can all be decomposed by heat. The manner in which potassium and sodium nitrate decompose has already been explained (Sec. 185). On heating nitrates of lead, copper, and barium, oxygen is also formed, but the residue is not a nitrite, but an oxide. The decomposition of lead nitrate is expressed by the equation:

$$2Pb(NO_3)_2 \longrightarrow 2PbO+4NO_2+O_2.$$

The gas, NO_2, formed during the reaction, is called *nitrogen peroxide.* Metallic nitrates can be formed by the action of nitric acid on metals, oxides, hydroxides, or carbonates. Silver nitrate is used in photography, the nitrates of lead, iron, and aluminium in dyeing, and those of barium and strontium for fireworks.

190. Tests for nitric acid and nitrates.—(1) If a piece of copper is dropped into nitric acid or into a nitrate mixed with concentrated sulphuric acid, brown fumes are produced.

(2) A concentrated solution of ferrous sulphate is shaken with nitric acid or with a solution of a nitrate, and the solution is cooled. A drop of this solution is then put on a sheet of glass which covers a piece of white paper, and a drop of concentrated sulphuric acid is placed beside the first drop. The formation of a brown colour where the two liquids meet is a certain and delicate test for a nitrate.

191. Commercial importance of nitric acid—Explosives.—Nitric acid is the basis of almost all explosives. Now, an *explosion* is due to the sudden release of gas under pressure. Accordingly, an explosive is usually a substance that, when it explodes, produces large quantities of gases and much heat; moreover, if these gases are confined within a small space, as in a shell, they produce great pressure which the container is not able to resist, and the contents are violently projected.

(1) *Gunpowder* has the following composition: 75 per cent. potassium nitrate, 10 per cent. sulphur, and 14 per cent. charcoal. The chief substances produced on explosion are carbon dioxide, nitrogen, and potassium sulphide; and since the latter substance is a solid a smoke is produced. Indeed, if any metal forms part of one of the ingredients of an explosive, its compounds will be almost always solids, and the explosive will not be smokeless.

(2) *Gun-cotton*, or *nitrocellulose*, is made by acting on cotton wool with nitric acid. It is a very powerful explosive used in torpedoes and mines.

(3) *Nitro-glycerine.*—All are familiar with the sweet syrupy liquid, glycerine, formed as a by-product in the manufacture of soap. When glycerine is acted on by nitric acid, nitro-glycerine is produced. It is an oily liquid and a dangerous explosive. *Dynamite* is composed of a fine earth impregnated with nitro-glycerine, the earth acting as a carrier which makes it less likely to explode and hence less dangerous to handle; the fine earth is frequently replaced by sawdust. *Smokeless powder*, or *cordite*, is composed of a mixture of gun-cotton and nitro-glycerine. Since each of the components of cordite is composed of carbon, hydrogen, oxygen, and nitrogen, only gases are formed during the explosion and hence no smoke is produced.

(4) *Picric Acid, or lyddite.*—Carbolic acid, which is so well known as a disinfectant, is a product obtained from coal-tar (Sec. 134). When carbolic acid is acted on by

nitric acid a yellow crystalline solid, picric acid, is produced, which is a violent explosive called by various names in different countries. In England it is called lyddite. It is used extensively in high-explosive shells, which played such an important part in the Great War. However, *trinitrotoluene*, another nitric acid product, is now largely replacing lyddite in high-explosive shells.

OXIDES OF NITROGEN

There are five oxides of nitrogen, three of which are anhydrides, corresponding to the three oxygen acids of nitrogen.

Name of oxide	Formula	Corresponding acid	Formula
Nitrous oxide.......	N_2O	Hyponitrous....	$H_2N_2O_2$
Nitric oxide.........	NO		
Nitrogen trioxide....	N_2O_3	Nitrous........	HNO_2
Nitrogen peroxide...	N_2O_4 or NO_2		
Nitrogen pentoxide..	N_2O_5	Nitric..........	HNO_3

All of these oxides are endothermic compounds.

192. Nitrous oxide.—Nitrous oxide is formed by heating ammonium nitrate:

$$NH_4NO_3 \longrightarrow N_2O+2H_2O.$$

It is a colourless gas, and since it is fairly soluble in water, it is best collected over hot water. Hyponitrous acid cannot be formed by dissolving nitrous oxide in water, as such a solution has no acid properties; but the fact that hyponitrous acid, on decomposition, breaks up into nitrous oxide and water would justify us in calling the oxide an anhydride:

$$H_2N_2O_2 \longrightarrow N_2O+H_2O.$$

The gas has been long known, having been prepared before oxygen. If it is inhaled it produces unconsciousness and hence is used much by dentists during the extracting of teeth. However, if it is inhaled in too great quantities, it causes death. But if it is inhaled with oxygen the effects are so remarkable that it has long been called "laughing gas", though the inhalation does not always cause the intoxicated person to laugh. For example, the late Sir Henry Roscoe described a chemical debauch at the close of a laboratory lesson, when all who wished became intoxicated with nitrous oxide. The laboratory assistant just sat on a box and made a series of the most excruciating grimaces; while Watt, the author of the great dictionary of chemistry, danced about in a high state of exhilaration, clicking his thumbs in great delight; on the other hand, Fox, a Quaker, desired to fight everybody and finally succeeded in pummeling an exciseman. Fortunately, the effects lasted only a few minutes, and when all came to, the Quaker was almost as surprised as the exciseman. For use as an anæsthetic the oxide is put up in the liquid form in cylinders.

This gas supports the combustion of wood, phosphorus, sulphur, etc., almost as brilliantly as oxygen:

$$C+2N_2O \longrightarrow CO_2+2N_2.$$

193. Nitric oxide.—Nitric oxide is best prepared by acting on copper with nitric acid diluted with an equal volume of water. We may consider the reaction as taking place in two stages; first, the copper and nitric acid react, the metal replacing the hydrogen:

$$2HNO_3+Cu \longrightarrow Cu(NO_3)_2+[_2H].$$

Then, the hydrogen reduces more of the acid:

$$2HNO_3+6H \longrightarrow 2NO+4H_2O.$$

As has been said already, this method of viewing reactions as taking place in several stages, is sometimes useful in connecting the reaction in the mind with other reactions but, of course, the whole reaction is a unit, and all that we really know are the reagents we begin with and those finally produced. Since there is no sign of hydrogen being present in any stage of the reaction we have written the symbol in square brackets [$_2$H].

Nitric oxide is a colourless gas, only slightly soluble in water, and very difficult to liquefy. Wood and sulphur will not burn in it, nor will phosphorus unless it is burning vigorously before it is brought into the gas. Its most characteristic property, however, is that of spontaneously uniting with oxygen to form a brown gas, nitrogen peroxide. Hence when a bottle of it is allowed to diffuse into the air, a brown vapour is produced, as the nitric oxide at once unites with the atmospheric oxygen. Indeed, this change in colour is an excellent test for both it and oxygen.

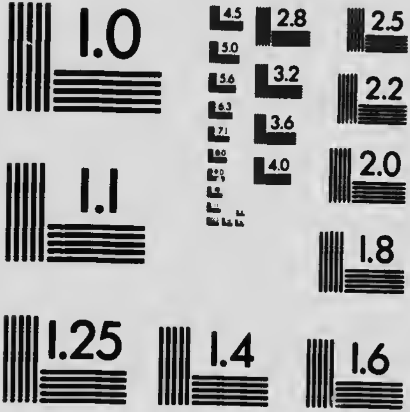
194. Nitrogen peroxide.—As has just been stated, nitrogen peroxide is the brown gas formed by the union of nitric oxide with oxygen. It is also formed when the nitrates of the heavier metals such as copper or lead are heated (Sec. 189). It dissolves readily in warm water, forming nitric acid and nitric oxide:

$$3NO_2+H_2O \longrightarrow 2HNO_3+NO.$$

If a jar partly filled with nitric oxide is collected over water and oxygen is gradually passed into it, the gas in the jar becomes coloured brown and, even though a gas is being added to it, it shrinks in volume. Priestley said when he first performed the experiment: "I hardly know any experiment that is more adapted to amaze and surprise than this, which exhibits a quantity of air (nitric oxide) which, as it were, devours a quantity of another kind of air (oxygen) half as large as itself". The explanation is, of course, that the nitrogen peroxide dissolves in the water as fast as it is formed.

MICROCOPY RESOLUTION TEST CHART

(ANSI and ISO TEST CHART No. 2)



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This gas acts in a remarkable manner with change of temperature. While below −10° C. it is a colourless crystalline solid; at this temperature it melts to a liquid which, on being steadily heated, first becomes pale greenish-yellow, then distinctly yellow, then orange, and at 22° C. boils, producing a yellowish-brown vapour which, with a further rise of temperature, becomes darker, and at 140° C. is almost opaque; at higher temperatures still it again becomes paler, and at 620° C. is colourless. As the colourless gas is cooled, it assumes all these colours in the reverse order. The light coloured gas has the formula N_2O_4, the gas begins to turn darker because the N_2O_4 begins to decompose into NO_2, and the substance of this formula is coloured deep brown:

$$N_2O_4 \rightarrow 2NO_2.$$

The more of this latter gas there is formed the more intense becomes the colour, so that at 150° C. the gas is all NO_2. Again, at higher temperatures the nitrogen peroxide decomposes into nitric oxide and oxygen, which are both colourless. The whole series of reactions that take place as the gas changes when heated, from light yellow through deep brown to a colourless gas, and the reverse reactions that take place when the colourless gas is cooled, are represented by the equation:

$$N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO+O_2.$$

195. The new method of manufacturing nitric acid.—The Chili saltpetre beds have been the great source of nitrates for the world. The increased demand for nitrates as fertilizers would indicate that that source of supply will in a measurable time be exhausted, and there has been great anxiety in industrial circles as to future supplies. Fortunately, during the last few years, chemists have solved the problem. Cavendish performed the following experiment in 1785: He arranged apparatus something like Figure 51. The goblets and inverted tube contained mercury, and the terminals of an electrical machine were dipped in the mercury in the goblets, then electric sparks were passed through the air column left in the upper part of the inverted tube, and soon a brown gas appeared. Water was then passed up above the mercury and the brown gas dissolved in it to form nitric acid. The reaction was as follows: The spark raised the temperature of the air through which it passed to such a high temperature that some of the oxygen and nitrogen united to form nitric oxide, which in the cooler part of the tube combined with more oxygen to form nitrogen peroxide, and this dissolved in water to form nitric acid. That experiment performed almost 150 years ago is just now beginning to bear fruit in the industrial world. For if air is made hot enough, its two components, oxygen and nitrogen, take fire and burn. The required heat is obtained in the arc between two electrical terminals which are inclosed in a tube. Through this arc air is forced, and the gases formed are passed into water or lime-water, when nitric acid or calcium nitrate is formed. As Britain controls the entire supply of Chili saltpetre, Germany, during the Great War, depended very largely on nitrate manufactured

Fig. 51.—Cavendish's Experiment for Converting Air into Nitric Acid
The goblets contain mercury.

electrically from air to produce her explosives and to fertilize her fields.

AMMONIA, NH_3

196. History.—Ammonia has been known from very early times, as it is formed naturally during organic decay, and its odour is common about stables. The name seems to have some connection with the temple of Ammon, a famous shrine in one of the oases of western Egypt, where perhaps ammonia was made by heating refuse matter. Undoubtedly it was prepared very early in Egypt by distilling the bones, hoofs, and horns of the native animals, and accordingly it was called spirits of hartshorn. Only solutions were known until Priestley succeeded in collecting the gas in his pneumatic trough over mercury.

197. Preparation.—Most organic matter contains nitrogen and hydrogen, and when it is destructively distilled these two elements combine to form ammonia, NH_3. The great source of supply, however, is coal, which, when distilled to produce illuminating gas, liberates great quantities of ammonia. This is dissolved in water to form ammonia solution.

In the laboratory it is usually prepared by mixing together ammonium chloride and slaked lime, and heating them:

$$2NH_4Cl+Ca(OH)_2 \longrightarrow CaCl_2+2NH_3+2H_2O.$$

Ammonium sulphate or nitrate may be substituted for the chloride, and sodium or potassium hydroxide may replace slaked lime. Another excellent method of preparing ammonia is by heating ammonia solution. This method is largely used in the laboratory. As the gas is lighter than air and soluble in water it must be collected by the displacement of air, or over mercury.

198. Properties.—Ammonia is a colourless gas with a pungent smell. It is more soluble in water than any other gas, 1 litre of water dissolving over 1100 litres of the gas. All the dissolved gas can be driven off by boiling the solution. The gas is readily converted into a liquid, and 1 gram of the latter, on evaporation, absorbs over 300 calories of heat, the heat of vaporization being greater than that of any other liquid except water. On account of its easy liquefaction and its great heat of vaporization, it is used very largely for producing cold and for refrigeration.

It neither burns in air nor supports combustion, but if a jet of it is lighted in oxygen it burns with a large yellow flame.

The apparatus illustrated in Figure 52 can be used to show this. The flask contains ammonia solution which is kept boiling. Oxygen is passed down into the flask; the mixture of gases, as it issues from the mouth of the flask, is ignited and continues to burn.

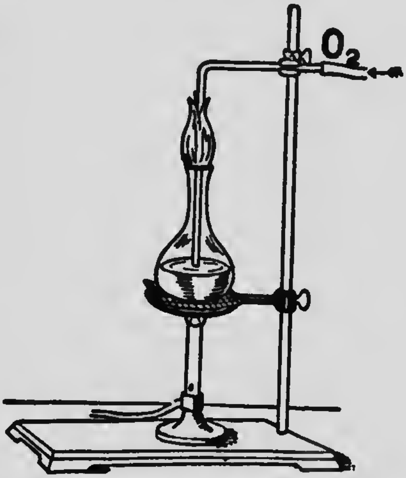

FIG. 52.—APPARATUS FOR BURNING AMMONIA

Ammonia water is heated in the flask and oxygen is passed in through the tube.

When electric sparks are passed through the gas for some time, a partial decomposition into the elements takes place; again, if electric sparks are passed through a mixture of nitrogen and hydrogen in the proportions in which they are present in ammonia, these gases combine partially to form ammonia. This is, accordingly, an excellent example of a reversible reaction that comes to equilibrium:

$$N_2+3H_2 \rightleftarrows 2NH_3.$$

For it matters not whether we start with the elements or the compound, when we pass electrical discharges through the gases for some time we obtain the same proportion of the three substances. Usually there is about 2 per cent. of ammonia. If, however, an acid is put in contact with the gases, then as quickly as ammonia is formed, it is absorbed, and, its concentration being kept at zero, the reaction proceeds until the elements have wholly combined.

199. Ammonia solution and ammonium salts.—A solution of ammonia in water, called *liquor ammoniæ*, is the form in which we are most familiar with the substance. This liquid neutralizes acids to form salts just as does sodium or potassium hydroxide, and the salts, in their properties, are very much like the corresponding salts of sodium and potassium. The following table shows the formulæ of some common salts formed in this way, with the corresponding sodium and potassium salts:

NH_4Cl	$NaCl$	KCl
NH_4NO_3	$NaNO_3$	KNO_3
$(NH_4)_2SO_4$	Na_2SO_4	K_2SO_4

The group NH_4 is a radicle (Sec. 84) called *ammonium*, and is very similar in its chemical action to sodium and potassium. Moreover, on account of the solution of ammonia acting quite similarly to solutions of potassium and sodium hydroxide and forming similar salts with acids, the formula is written similarly to that of sodium and potassium hydroxide, NH_4OH. Ammonium hydroxide solution, just like the other alkalies, feels smooth to the touch and turns red litmus blue. Usually, however, pure ammonium hydroxide cannot be obtained by evaporating the solution as can the hydroxides of sodium and potassium. Nevertheless, in 1909, the hydroxide NH_4OH, was obtained in the form of needle-shaped crystals, but only at the very low temperature of −91° C.

When heated, the ammonium salts are all volatile; some (the nitrate for example) decompose into constituents that do not unite again on cooling. Others change into substances that unite again as the temperature is lowered, and are said to *dissociate.* Examples of this are ammonium chloride, which dissociates as follows:

$$NH_4Cl \rightleftarrows NH_3+HCl,$$

and ammonium carbonate, used in smelling salts, which dissociates at ordinary temperatures into ammonia, water, and carbon dioxide.

200. Commercial importance of ammonia and ammonium salts.—The "gas liquor" from the gas-plant is usually heated, and the ammonia that comes off is passed into sulphuric acid to form ammonium sulphate. This salt forms the basis from which the other ammonium salts are formed. As liquor ammoniæ or ammonia solution is an excellent solvent for oils and grease, it is used in the home for cleaning. Household ammonia is in fact only a dilute solution of ammonia with a small amount of soap dissolved in it. Ammonia is also used in the preparation of alum, soda, aniline colours, and indigo. By far the most important salt of ammonia, however, is ammonium sulphate, extensively used as a fertilizer.

201. Test for ammonium compounds.—Any ammonium salt, when mixed with potassium hydroxide and heated, gives off ammonia, which can be detected by its odour.

NITROGEN CHLORIDE

202. Nitrogen chloride.—Nitrogen chloride is probably the most dangerous explosive known, as it detonates with the slightest disturbance, or apparently with none at all. When Dulong, who first prepared this liquid, was holding the tube containing it in one hand, it exploded with terrific violence, blowing out one eye and shattering three fingers. He pluckily continued his investigation and resolved to keep all knowledge of such a dangerous substance to himself, in order that nobody else should be injured by it. Faraday, a few years later, was knocked senseless while experimenting with the same substance. Fortunately he had a glass mask on at the time, so that his chief wound was due to some glass cutting his fingers.

QUESTIONS

1. Why cannot nitric acid be used with metals to prepare hydrogen?

2. What reactions that come to equilibrium take place when concentrated sulphuric acid is poured upon sodium nitrate? In which direction is the equilibrium displaced by heating the solution?

3. State the reason why hydrochloric acid cannot replace sulphuric acid in the preparation of nitric acid from Chili saltpetre.

4. Which of the following could be used for drying ammonia: sulphuric acid, phosphorus pentoxide, calcium oxide, potassium hydroxide? Give reasons.

5. If 1 gram of water dissolves 1298 c.c. of ammonia at N.T.P., what weight of ammonia will it require to saturate 5 grams of water?

6. How many litres of oxygen are required when 10 litres of nitric oxide are converted into nitrogen peroxide?

7. How many grams of nitrous oxide can be prepared from 20 grams of ammonium nitrate? What volume does the gas occupy at 10° C. and 950 mm. pressure?

8. What is the weight of 112 litres of ammonia measured at N.T.P.? What volume at N.T.P. will 32 grams of ammonia occupy?

9. How can nitrous and nitric oxide be distinguished? How can oxygen and nitrous oxide be distinguished?

10. If a liquid is known to be a solution of either sulphuric,

nitric, or hydrochloric acid, how would you tell which it is? Give different methods of identifying it.

11. Cavendish, by passing electric sparks through air and then dissolving the gas produced in water, obtained nitric acid. Write the equations expressing the reactions.

12. Starting with soft coal and sulphuric acid, state the process by which ammonium sulphate could be produced.

13. Write formulæ for the following substances: ammonium sulphate, ammonium phosphate, ammonium sulphite, ammonium perchlorate, ammonium hydroxide, ammonium iodide.

14. Write names for the substances having the following formulæ: NH_4NO_3, $(NH_4)_3PO_4$, NH_4HCO_3, $(NH_4)_2SO_3$, NH_4ClO, NH_4KCO_3.

CHAPTER XVIII

THE ALKALI METALS

"A small piece of potash . . . was placed on insulated platina connected with the negative side of the battery . . and a platina wire communicating with the positive side was brought in contact with the upper surface of the alkali . . . There was a violent effervescence at the upper surface; at the lower . . . small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame."

—*Sir Humphry Davy, 1807*

203. Elements are divided into groups.—Up to the present we have considered each element as quite distinct in its properties from others, except that in describing sulphur we stated that it resembled oxygen somewhat in its action (Sec. 150). If each element were unrelated in its properties to all the others, the study of the elements would put a very severe tax on the memory, and chemistry would consist of a great mass of disconnected facts, instead of the groups of correlated facts that one looks for in a science. But happily such is not the case, for all the elements can be arranged in groups, the members of each group closely resembling one another in their properties; so that if one learns the chemistry of a single member of each group he can successfully prophecy the chemistry of the other members of the group. Up to the present, however, we have been studying only members of different groups, except in the case of sulphur and oxygen; now, however, we shall study two members belonging to the same group, and it will be quite evident how closely they resemble each other.

204. The group of the alkalies.—The five elements of the alkali group are metals, and the following table shows how certain properties change regularly with increase of atomic weight:

Name	Atomic weight	Specific gravity	Melting-point	Boiling-point
Lithium.....	7.0	0.53	186° C.	1400° C.
Sodium.....	23.0	0.97	97° C.	877° C.
Potassium...	39.1	0.86	62.5° C.	700° C.
Rubidium...	85.5	1.53	38.5° C.	696° C.
Caesium.....	132.8	1.87	26.5° C.	670° C.

All these elements are silvery white, can easily be cut by a knife, decompose water when thrown upon it, and burn in oxygen. Furthermore, they are all univalent, their hydroxides are strongly basic, their salts are mostly white, soluble in water, and those of the same acid closely resemble one another in many respects. If the names of the salts with a list of their properties were arranged in a table like the one given above, it would be found that there would be as regular a gradation as there is for the elements themselves, with occasional exceptions like the specific gravity of potassium in the above list. Hence, if one knows the properties of one of the elements and the positions of the others in the group, the properties of all can be foretold with a fair degree of certainty. We shall study the two most important members of the group, *sodium* and *potassium.*

SODIUM

205. Historical.—Sodium hydroxide was long considered to be an element, and it was not until 1807, when Sir Humphry Davy performed his epoch-making experiment, described in his own words at the head of this chapter, that this element together with potassium was obtained. He electrolysed a small piece of sodium hydroxide and the metal appeared at the cathode.

206. Preparation.—Sodium is prepared in a manner very similar to that in which Davy originally prepared it; for the hydroxide is fused and then electrolysed, when oxygen collects at the anode and hydrogen and sodium at the cathode.

207. Properties of the metal.—Sodium is a soft metal of a silvery-white metallic lustre, which quickly oxidizes in the air to form one of the oxides; its action on water has been studied already (Sec. 41). As the density of the vapour is about 11.5 times as great as that of hydrogen, its molecular formula in the form of a gas is Na.

208. Oxides.—There are two oxides, Na_2O and Na_2O_2; the latter, called sodium peroxide, is of most importance. When sodium burns in air a mixture of the two oxides is formed, but when oxygen is passed over heated sodium it is largely the peroxide that is formed. The action of this latter oxide on water has been already studied (Sec. 15). If, however, the temperature of the water, which reacts with the peroxide, is kept low, not oxygen, but hydrogen peroxide is produced:

$$Na_2O_2+2H_2O \longrightarrow H_2O_2+2NaOH.$$

209. Sodium hydroxide.—This strong base, commonly called caustic soda, has been mentioned frequently already. When sodium acts on water a solution of it is formed. It is manufactured in several ways. (1) By the electrolysis of a solution of common salt. This method has been fully described in Section 116. (2) By acting on a solution of sodium carbonate with slaked lime:

$$Na_2CO_3+Ca(OH)_2 \longrightarrow 2NaOH+CaCO_3.$$

SIR HUMPHRY DAVY (1778-1829)

English chemist and physicist. After an apprenticeship with a surgeon-apothecary, he turned to chemistry and in time became a professor in the Royal Institution. In 1807 the French Institute awarded him the Napoleon prize of three thousand francs for his experiments made in electricity. In 1818 he was created a baronet, and in 1820 he was elected President of the Royal Society. His great success in chemical research was due not so much to his tireless investigations as to his highly imaginative mind. He discovered that alkalies and earths are compound substances formed by the union of oxygen with metallic bases; he decomposed soda, baryta, strontia, lime, and magnesia, thus discovering the metals sodium, barium, strontium, calcium, and magnesium. He won lasting fame by the invention of the safety-lamp for miners.

As the calcium carbonate is insoluble, and the sodium hydroxide is very soluble, they can be readily separated by filtration. Sodium hydroxide is generally sold for use in the laboratory in the form of white sticks, which not only dissolve in water but, if exposed to the air, rapidly deliquesce and in time entirely dissolve in the absorbed water. It is a dangerous substance, as it corrodes the flesh and injures clothing. Great quantities of it are required for the formation of ordinary soap. It is now manufactured at Windsor, Ontario, where a large establishment has recently been constructed, in which caustic soda, together with chloride of lime, is prepared by the electrolysis of salt solution.

210. Manufacture of soap.—Soap is a sodium salt of certain acids, called fatty acids, obtained from fats. The reaction may be expressed in this way:

Fat+sodium hydroxide⟶soap+glycerine.

The fat is first melted by means of steam in large vats, then sodium hydroxide is added and the mixture heated for from one to two days, when a strong brine is added and, as soap is insoluble in brine, the former rises to the top, while the glycerine remains in the brine. The soap is now skimmed off, and after purification and perfuming, is made into cakes or bars.

211. Sodium carbonate.—After sulphuric acid, sodium carbonate is the most important chemical. When it is mentioned that almost all glass and soap require it for their manufacture, it is easy to understand what vast quantities of it are used. Besides, it is used as washing-soda and for making baking-soda and baking-powder, as well as for making many cleaners used in the household. Almost up to the nineteenth century it was largely prepared by burning sea plants. During the Napoleonic wars, however, as France was cut off from her source of supplies, sodium and potassium carbonate being largely prepared in Britain and America, Napoleon offered a prize of $20,000 to the chemist who would discover a commercial method of preparing it from common salt. N. Leblanc won the prize, and his method has been largely used ever since. However, about 1870, Solvay, a Belgian, perfected a more economical method which has partially driven the Leblanc process out of the field. Again, within recent years the electrolytic method threatens to make inroads upon both the older methods.

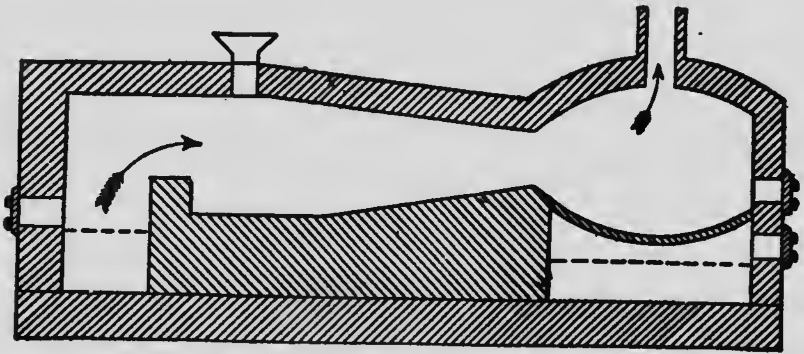

FIG. 53.—BLACK ASH FURNACE

The salt and sulphuric acid are placed in the basin on the right and later are raked forward on the reverberatory furnace. The hydrogen chloride escapes by the chimneys above.

(*a*) *Leblanc process.* This depends on the following reactions:

$$2NaCl+H_2SO_4\longrightarrow Na_2SO_4+2HCl.$$
$$Na_2SO_4+2C\longrightarrow Na_2S+2CO_2.$$
$$Na_2S+CaCO_3\longrightarrow NaCO_3+CaS.$$

The process takes place in two stages. The mixture of common salt and sulphuric acid is placed in a basin (Fig. 53) under which is a furnace. The hydrochloric acid is partially driven off here, and then the mixture is raked forward, where it is subjected to a much more intense heat from the furnace, until only sodium sulphate is left.

The sodium sulphate, called salt-cake, is mixed thoroughly with coal and lime and transferred by means of a car, (Fig. 54) to a cylinder to be heated. The furnace is at the left; the burning gases from the fuel pass through the cylinder to the right, which is kept rotating so that the ingredients may be thoroughly mixed. Afterwards, the mixture, called black ash, is taken out by means of the car beneath the cylinder. As the calcium sulphide is insoluble in water, the sodium carbonate is separated by dissolving it in water. There are several valuable by-products from this process: Hydrochloric acid, which is used for manufacturing chlorine and bleaching-powder, and sulphur, which is extracted from the calcium sulphide and utilized to manufacture sulphuric acid. A factory used for manufacturing soda by Leblanc's process is called an *alkali factory*, and is usually a very large establishment with buildings for manufacturing chlorine, bleaching-powder, sulphuric acid, and soda.

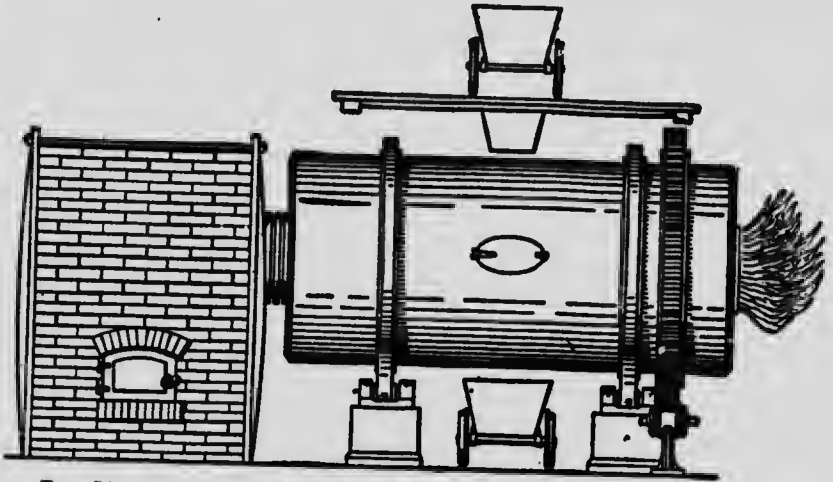

FIG. 54.—ROTATING FURNACE IN WHICH SALT-CAKE IS CONVERTED INTO BLACK ASH

The furnace is at the left. A car above the rotating cylinder delivers the salt-cake, and the car below receives the black ash.

(*b*) *Solvay's Process.*—In this process ammonia and carbon dioxide are passed into a strong solution of common salt, and sodium bi-carbonate, $NaHCO_3$, as it is only sparingly soluble in water, settles to the bottom. By treating with lime the ammonium chloride remaining in the solution, the ammonia is driven off and can be used over and over again. Again, if the sodium bicarbonate is heated, it is converted into sodium carbonate and carbon dioxide:

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O.$$

The carbon dioxide can again be utilized in manufacturing more soda. Accordingly, in this process the only chemicals that have to be renewed are sodium chloride and a part of the carbon dioxide, which are both cheap.

This method can be illustrated in the laboratory by making a saturated solution of common salt in ammonium hydroxide solution, and passing carbon dioxide into the solution for an hour, when a white precipitate of sodium bicarbonate will settle to the bottom.

(*c*) The *electrolytic process.* This consists in making sodium hydroxide by the method already described in Section 209, and treating a solution of it with carbon dioxide:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O.$$

212. Sodium chloride and **sodium nitrate** have been already dealt with in Sections 96–99, and 183.

The phosphate, sulphite, bromide, iodide, and chlorate, are white salts, soluble in water, which can be prepared from the carbonate by adding the corresponding acids.

213. Test for sodium.—Sodium or any of its salts when placed in a colourless flame gives it an intense yellow colour.

POTASSIUM

214. The Stassfurt salt beds.—Near the little German town of Stassfurt, about 80 miles south-west of Berlin, occur the most remarkable salt beds in the world. Figure 55 is a representation of a section through them. They consist of a number of layers with a bed of rock-salt (sodium chloride) of immense thickness at the bottom. The upper layer is *carnallite*, composed of potassium and magnesium chlorides; the other layers contain, in addition to these, magnesium, potassium, and calcium sulphates. They all contain large quantities of common salt. The total thickness of all the layers is almost half a mile, and the area they cover is quite unknown. All the layers are pure white except the carnallite, which is of a delicate pink. In 1850 a shaft was begun through the upper sandstones and clays to the salts and was only completed after five years. In the early working

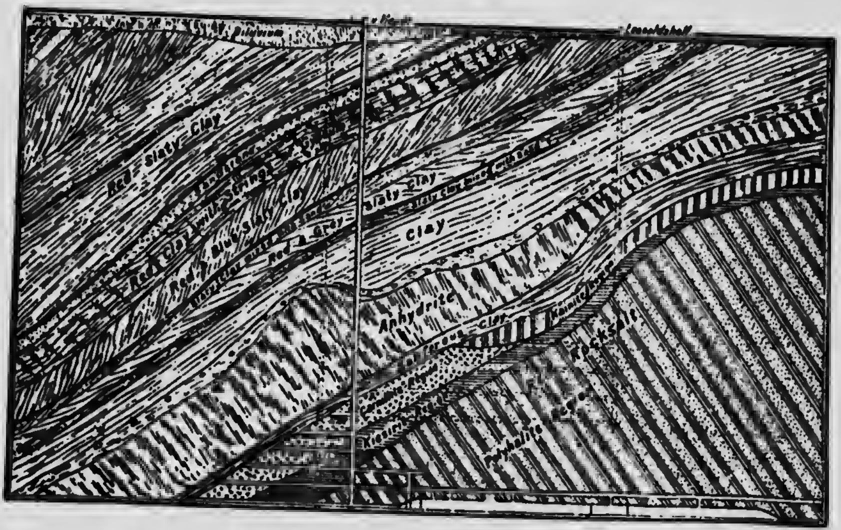

FIG. 55.—SECTION THROUGH STASSFURT SALT BEDS
One shaft with lateral tunnels is indicated.

of the mine, the substances composing the upper layers were discarded as refuse, only the rock-salt being mined. Later, however, the carnallite began to be utilized as a source of potassium chloride. Indeed, to-day what was formerly refuse is most valuable, as the carnallite in the top layer is the source of almost all the world's supply of potassium salts. Consequently, Germany, because she owns the Stassfurt salt bed, has had almost complete control of the manufacture of potassium salts. This is the reason that when the Great War broke out the prices of all potassium salts increased with a bound. At once, other nations had to look about for sources of potassium, and were compelled to resort to pre-Stassfurt methods of obtaining potassium salts. Again, the same beds supplied the salts from which the Germans manufactured the poisonous gas, chlorine, used as a weapon of attack in the Great War. As the salts of these beds are identical with those found in sea water, they were undoubtedly formed by the evaporation of a great sea, which process must have taken place under exceptional circumstances to have produced a bed of such immense thickness.

215. Other sources of potassium.—In the pre-Stassfurt days, wood ashes were a great source of potassium salts, and Canada was an important producer. In Upper and Lower Canada, as they were then called, wood was piled in great mounds and burned in order to obtain the ashes, from which was dissolved the *potash* or potassium carbonate. Another rather remarkable source of potassium salts is the oily residue found adhering to the wool of sheep. This oil must be removed before the wool can be further utilized, and from the oil is produced potassium carbonate. Further, in the massive rocks of Canada we have vast quantities of potassium salts in the form of silicates, beside which Stassfurt dwindles into insignificance; but unfortunately no commercial method of utilizing these for the extraction of potassium has yet been discovered, though at the present time much investigation is being carried on in order to accomplish this result.

216. Potassium salts.—Potassium, its oxides, hydroxides, and salts, so closely resemble sodium and its corresponding compounds that no detailed description of potassium and its compounds is necessary. Potassium chloride, though found in great quantities at Stassfurt, is much less abundant and more difficult to mine than rocksalt; and as the other salts of each are mostly derived from the chlorides, the price of potassium salts is much higher than the price of those of sodium. Furthermore, as the atomic weight of sodium is only a little more than half that of potassium, sodium, weight for weight, will go farther than potassium in chemical reactions.

The most important compounds of potassium are the hydroxide, carbonate, chloride, chlorate, and nitrate.

217. Potassium hydroxide.—Potassium hydroxide, usually called caustic potash, is a white deliquescent solid, very soluble in water. It is used in large quantities for making soap. But while the soap produced by sodium hydroxide is hard and can be made into bars, that produced from caustic potash remains gelatinous, and is called *soft soap*. It is frequently made at home by dissolving the potash out of wood ashes to form *lye*, which is boiled with fats.

218. Potassium carbonate.—This salt is prepared from wood ashes, the oil from sheep's wool, and from potassium chloride. It is used largely for making soap and glass.

219. Potassium nitrate or saltpetre has been already fully discussed (Sec. 184). It is now produced in large quantities by the action of potassium chloride on sodium nitrate. When these two react, sodium chloride and potassium nitrate are formed. Now, at 100° C., 100 c.c. of water dissolve 246 grams of potassium nitrate and only 39 grams of sodium chloride. Consequently, when the liquid is evaporated, the sodium chloride separates out from the boiling liquid on account of its small solubility. While still hot, the clear liquid is drawn off and allowed to cool. Since at 10° C., 100 c.c. of water dissolve not only 13 grams of potassium nitrate, but dissolve 36 grams of sodium chloride—almost as much as the boiling liquid did—when the solution cools almost all the potassium nitrate settles to the bottom and is collected. Thus two soluble salts are separated by crystallization, largely because the solubility of sodium chloride is about the same in hot and in cold water.

220. Test for potassium.—A potassium salt when placed in a colourless flame gives it a violet tinge. However, this colour is frequently masked by a trace of sodium.

QUESTIONS

1. Which do you consider the most important compound of sodium? Of potassium? Why?

2. How much sodium hydroxide could be produced by the electrolysis of 1000 pounds of salt? (Sec. 116)

3. Explain how soda can be prepared from sodium. Write the equations. Why is it not a good commercial method of preparing soda?

4. Potassium nitrate is prepared by acting on sodium nitrate with potassium chloride. By a study of the solubility curves (Fig. 26) of these salts and their products determine how these two salts can be separated.

5. Why is sodium nitrate rather than potassium nitrate used for the preparation of nitric acid?

6. Why is potassium nitrate rather than sodium nitrate used for gunpowder?

7. What is the difference between soda and caustic soda; between baking-soda and washing-soda; between hard soap and soft soap; between baking-soda and baking-powder; between potashes and caustic potash?

8. How would you distinguish sodium chloride, potassium chloride, and ammonium chloride ?

9. How would you separate a mixture of sodium and ammonium chloride? (Sec. 199)

10. How can you prepare sodium hydroxide from sodium carbonate?.

11. Why are the metals, sodium and potassium, kept under kerosene?

12. State the three changes that take place in sodium when exposed to the air.

13. What compounds of sodium and of potassium can be used to dry gases?

14. Why is sodium carbonate used in cleaning floors? Why is the hydroxide not used?

15. How can you prove that plants contain potassium compounds?

16. In the Solvay process of manufacturing soda, why is the bicarbonate obtained first rather than the carbonate?

17. Why are sodium carbonate and bicarbonate used in washing and baking rather than the potassium compounds?

18. Which will neutralize the greater quantity of acid, a gram of sodium hydroxide or of potassium hydroxide?

19. You are given a white powder which is either washing-soda or baking-soda. How can you tell which it is?

20. How can you distinguish Chili saltpetre from ordinary saltpetre?

CHAPTER XIX

CALCIUM

221. Occurrence.—As calcium readily reacts with either air or water, it is never found in nature except combined, but in combination it is one of the most abundant of the elements. Indeed, of the metals only iron and aluminium form a larger part of the earth's crust. Limestone, $CaCO_3$, forms vast rock masses in many parts of the world, while gypsum, $CaSO_4.2H_2O$, is also very abundant. Calcium phosphate, a valuable mineral, is also widely distributed.

222. Preparation.—Up to 1904 calcium was a laboratory curiosity, worth about five hundred and fifty dollars a pound. But by the end of 1905 the price had dropped to three dollars a pound, and now it can be purchased for less than one dollar a pound. This rapid decrease in price is due to the fact that a new and easy method of preparation was discovered. Although Sir Humphry Davy prepared it shortly after he had prepared sodium and potassium, he was never successful in freeing it from mercury. In the modern process, illustrated in Figure 56, calcium chloride is placed in a graphite crucible, which forms the anode, while a bar of iron the end of which is immersed in the fused salt forms the cathode. The height of the iron cathode is adjusted by a screw. All the chloride, except the part at the bottom, is kept fused. This lower part, however, is kept cool by the circulation of water in the pipes shown in the Figure. On passing a current the molten calcium floats to the top of the melted salt, and as it collects on the surface of the iron the latter is raised so as to keep the bottom of the calcium just in contact with the fused chloride. In this way an irregular bar of calcium is gradually formed on the bottom of the iron cathode.

223. Properties.—Calcium is slightly harder than lead and, like sodium, is acted on by water, though not so vigorously. It usually acts as a bivalent element. Though up to the present calcium has no application in chemical industry, there is a strong probability that a metal so cheap will prove useful in the future. Some of its compounds have been already discussed, as the carbonate (Sec. 137), hypochlorite (Sec. 114), oxide, and hydroxide (Sec. 137).

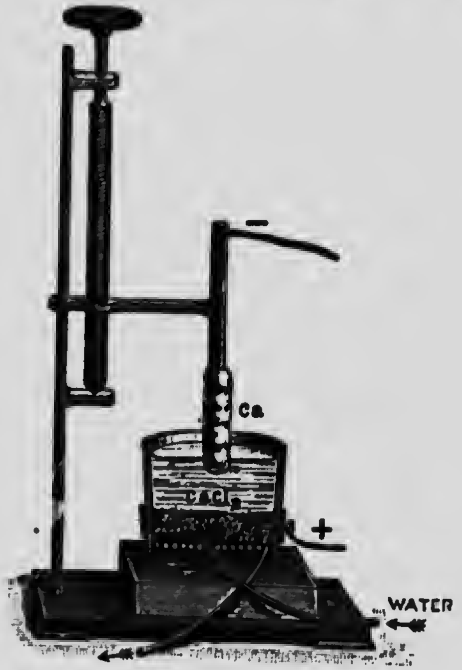

FIG. 56.—APPARATUS FOR PRODUCING CALCIUM

224. Calcium sulphate.—A crystalline substance, whose composition is represented by the formula $CaSO_4.2H_2O$, is called gypsum. As calcium sulphate is a component of sea-water it is usually found associated with salt beds. When it is heated to about 100° C. it loses part of its water, and at about 120° C. it changes into a fine white powder, whose composition is represented by the formula $(CaSO_4)_2.H_2O$. This powder, which is called *plaster of Paris*, is of great commercial importance. When water is added, it forms a white pasty mass which, in the course of ten minutes, sets to a hard, firm solid. Since it expands slightly in setting it is largely used in making casts, for, on hardening, every crevice in the mould is filled. In the setting process the plaster of Paris, by combining with the requisite amount of water, changes back to crystals of gypsum. This reaction may be expressed by the following equation:

$$2CaSO_4.H_2O+3H_2O \longrightarrow 2(CaSO_4.2H_2O).$$

Besides this, plaster of Paris is used as a cement and for forming the outer coat of plaster on walls. Again, gypsum is ground into a powder and used as a fertilizer called ***land-plaster***. Gypsum is only very slightly soluble in water.

225. Calcium carbide.—This substance, which has been already described (Sec. 131), is produced by heating in the electric furnace a mixture of quicklime and hard coal:

$$CaO+3C \longrightarrow CaC_2+CO.$$

Calcium carbide is manufactured in large quantities at Merritton and Welland in Ontario, and also in the Province of Quebec. Until quite recently it was used almost entirely for the production of acetylene gas; now large quantities of it are prepared to be further manufactured into calcium cyanamide by absorbing the nitrogen of the air.

226. Calcium phosphate.—This mineral is widely distributed, and when acted on by sulphuric acid, forms *superphosphate of lime*, a very valuable fertilizer. Calcium phosphate has been recently discovered in western Alberta, and, if found in quantity, should prove of great value to the Western farmer.

227. Tests for calcium.—1. A salt of calcium moistened with hydrochloric acid and put in a colourless flame, tinges it light red.

2. Sodium carbonate solution gives a white precipitate with a solution of a calcium salt.

3. Sulphuric acid gives a white precipitate with a solution of a calcium salt, unless the latter solution is very weak.

CHAPTER XX

THE HALOGENS—BROMINE AND IODINE

228. The halogen group.—This group includes chlorine, bromine (brō′-min), iodine (ī′-o-din), and fluorine (flu′-o-rin). The name halogen, meaning a "producer of salt", was given to these elements because they combine with metals to produce salt; that is, the salts found in the sea. The first three are intimately connected with the sea, as they are found in compounds in sea salt and also in the plants and animals that live in the sea; indeed, the main source of all of them is either the sea directly, or salt beds whose salt was formerly found in the sea.

Chlorine has already been treated, and the other members of the group resemble it closely in their properties and compounds. We will first study the chemistry of each element and then compare the members of the group.

BROMINE

229. Properties.—Bromine, at ordinary temperature, is a heavy liquid. It is the only non-metallic element in the liquid state, just as mercury is the only liquid element among the metals. Since it vaporizes at ordinary temperature, it rapidly escapes as brown fumes from an open vessel. The vapour has an unpleasant odour which has given it its name, from *bromos*, stench. As it is very irritating to the throat and eyes, it should be handled in the laboratory with great care.

It is not very soluble in water, the saturated solution containing only about 3 to 4 per cent. of bromine. It is moderately soluble, however, in alcohol, ether, chloroform, and carbon bisulphide, giving a characteristic brown solution. Like chlorine, it unites readily with many of the elements and acts as a bleacher. The vapour density of bromine would indicate that its molecular formula is Br_2.

230. Preparation.—There are several methods by which it can be prepared. One consists in acting on a mixture of manganese dioxide and sodium or potassium bromide, with concentrated sulphuric acid. The reactions are similar to those used for the preparation of chlorine (Sec. 107), except that the two operations must be performed together.

Commercially the above method is not used. The world's supply of bromine at present comes from two sources, the Stassfurt salt beds, and salt springs in the states of Ohio and Michigan. In both regions the element is prepared by passing chlorine through a solution of magnesium bromide:

$$Cl_2 + MgBr_2 \longrightarrow MgCl_2 + Br_2.$$

231. Hydrogen bromide is quite similar to the corresponding chlorine compound. Bromine and hydrogen combine readily to form hydrogen bromide, although they do not unite so vigorously as chlorine and hydrogen. Hydrogen bromide is a gas very soluble in water, the solution being a strong acid, hydrobromic acid, which reacts with metals, their oxides and carbonates, to form the corresponding salts, the bromides. It can not readily be produced, however, by acting on a metallic bromide with sulphuric acid, as the hydrogen of part of the hydrogen bromide formed attacks the sulphuric acid and reduces it to sulphur dioxide, while the bromine is liberated. This indicates a characteristic of hydrogen bromide, namely, its tendency to give up its hydrogen readily to reduce other substances containing oxygen.

232. Other bromine compounds.—Bromine also forms a series of oxygen acids and corresponding salts analogous to those of chlorine. Hypobromous acid has the formula $HBrO$, bromous acid is $HBrO_2$, bromic acid $HBrO_3$, perbromic acid $HBrO_4$; there is some doubt, however, as to whether the last acid has been prepared, but its salts are well known.

IODINE

233. Occurrence and preparation.—Iodine occurs in very small quantities in sea-water, but in much larger quantities in certain seaweeds that are washed up on the beach after storms. For many years these weeds were the chief source of iodine, and even now the seaweeds are gathered to a small extent in Scotland, Ireland, and France, burned, and the iodine extracted from the iodides in the ashes by means of sulphuric acid and manganese dioxide. In recent years, however, this source has been largely supplanted by the Chili nitre beds, already described. In Chili the *mother-liquors*, left after the crystallization of sodium nitrate, contain sodium iodate, from which iodine is easily extracted. From this source, indeed, it would be very easy to produce five times the quantity of iodine that is at present manufactured, but only enough is extracted for the world's supply, which is limited.

234. Properties.—Iodine is a black, flaky, lustrous solid. When heated it vaporizes without melting, such a process being called *sublimation*. The vapour is coloured violet, and it is from this property that the element received its name, which is derived from the Greek word *ioeides*, meaning "like a violet". Though almost insoluble in water, it is very soluble in alcohol, ether, aqueous potassium iodide, chloroform, and carbon bisulphide. The solutions in the first three liquids are brown, while in the latter two they are a beautiful violet, reminding one of the vapour. Since the slightest trace of iodine has the property of turning starch paste intensely blue, this is a very delicate test for free iodine. Its formula in the form of a gas at low temperature is I_2, while at higher temperatures it is I.

235. Compounds of iodine.—Iodine forms hydrogen iodide, HI; iodic acid, HIO_3; and periodic acid, HIO_4; all similar to the corresponding chlorine and bromine compounds. Hydrogen iodide is not so stable as hydrogen chloride, being easily decomposed by heat, and in sunlight its solution in water rapidly liberates iodine.

236. Uses of bromine and iodine.—These elements or their salts are used extensively in photography, in the dye industry, and in medicine.

237. Chlorides, bromides, and iodides.—The salts of the other halogen elements corresponding to the chlorides are quite similar to the latter, all giving insoluble salts with silver nitrate. Solutions of the bromides and iodides are decomposed by chlorine, liberating bromine and iodine:

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2,$$
$$2KI + Cl_2 \rightarrow 2KCl + I_2.$$

Bromine also liberates iodine from the iodides:

$$2KI + Br_2 \rightarrow 2KBr + I_2.$$

238. Comparison of the halogens.—We stated, on comparing the alkali group of elements, that there was a regular gradation of properties as the atomic weights increased in that group, and the comparative tables of properties below will show this gradation still more markedly in the case of the halogen group.

Property	Chlorine	Bromine	Iodine
Atomic weight......	35.5	80	127
State at ordinary temperature....	gas	liquid	solid
Melting-point......	–102° C.	–7.3° C.	114° C.
Boiling-point.......	–33° C.	60° C. (about)	183° C.
Specific gravity.....	1.55 (liquid)	3.19 (liquid)	5 (solid)
Colour of gas......	greenish	brownish	violet

This similarity extends also to the compounds, as the following table of the properties of the haloid acids shows:

Property	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Iodide
Molecular weight.........	36.5	81	128
Boiling-point.............	–83.7°C.	–64.9°C.	–34.1° C.
Melting-point............	–116° C.	–87° C.	–51° C.
Solubility in water........	42%	49%	57%
Boiling-point of solution...	110° C.	126° C.	127°C.
Dissociation begins at.....	1500° C.	800° C.	180° C.
Potassium salt melts at....	790° C.	750° C.	705° C.
Solubility of silver salt....	0.016%	0.00084%	0.000028%
Solubility of calcium salt..	42.7	58.8	67.6

QUESTIONS

1. Which decomposes at the lowest temperature, hydrogen chloride, hydrogen bromine, or hydrogen iodide?

2. Iodized starch paper is made by soaking absorbent paper in starch paste with a little potassium iodide in it. What would be the colour of the paper? If the paper were dipped in chlorine water, what colour would it turn? Explain and try the experiment.

3. Write the equation for the union of hydrogen with bromine vapour, Br_2. If 100 c.c. of hydrogen are used, how many cubic centimetres of hydrogen bromide would be produced?

4. If a mixture of sodium chloride and iodide were given you, how would you prove the mixture contains both a chloride and an iodide?

5. How would you distinguish bromine vapour from nitrogen peroxide?

6. Give the derivation of the names of the halogen elements.

7. How can you distinguish between a chloride, a bromide, and an iodide?

8. How many grams of magnesium bromide are necessary to produce 150 grams of bromine, when it is decomposed by chlorine? What volume of chlorine gas at N.T.P. is necessary to liberate the bromine?

9. How can bromine be obtained from hydrobromic acid? Write the equation?

10. In a class in botany it is required to find whether a leaf contains starch. Suggest a method of carrying out the test.

11. Write formulæ for the following: aluminium bromide, mercuric iodide, calcium bromate, potassium periodate, ferric bromide, phosphorous bromide, phosphoric bromide, sodium hypoiodite, magnesium perbromate.

12. Write names for the substances represented by the following formulæ: HgI, HgI_2, $KBrO_4$, $Ca(IO_3)_2$, $AlBr_3$, $SbCl_3$, $SbCl_5$, $Mg(BrO)_2$, HI, NCl_3, Cl_2O.

13. Bromine reacts with zinc, phosphorus, and potassium. Write the probable equations.

14. If iodine became mixed with sand, how could the two be separated?

15. What laboratory method is equally good for the preparation of chlorine, bromine, and iodine?

16. How large a flask may be filled with bromine vapour at normal pressure when 10 grams of bromine are put in a flask and the latter immersed in boiling water?

CHAPTER XXI

OZONE AND HYDROGEN PEROXIDE

239. Ozone.—Frequently when an arc lamp is turned on or a statical electrical machine is made to spark, the surrounding air acquires a peculiar odour. While this phenomenon was observed almost 150 years ago, it was many years later before it was ascertained that the odour was due to the formation of a peculiar substance. The substance that produced the odour was called *ozone* (*ozo*, to smell).

Ozone can be prepared in a variety of ways. When clean phosphorus is in contact with moist air, traces of it are formed. As the oxygen rises from the anode when acidulated water is being electrolysed, quantities of ozone are mixed with it. The apparatus used to form it in large quantities is shown in Figure 57. It consists of two concentric glass tubes, A and B, with metallic coatings. These coatings are connected with the terminals of an induction coil, by means of which a silent discharge is passed between the inner and the outer tube. When oxygen is passed through the space between the tubes, part of it is converted into ozone ; which, as it bubbles through the solution of potassium oxide at C, turns the liquid brown. This reaction is a test for ozone.

240. Properties of ozone.—Ozone is a gas which, as ordinarily prepared, is mixed with oxygen. But it has recently been converted into a beautiful indigo-coloured liquid. It can be converted into oxygen and can be formed out of oxygen without change of weight, therefore it must be an allotrope of this element. Besides, as its density is 1½ times that of oxygen, its formula must be O_3, and the equation expressing the reaction is

$$3O_2 \longleftrightarrow 2O_3,$$

for since by heating the ozone it is converted into oxygen, the reaction is reversible. Ozone is an excellent oxidizing agent. Hence if silver is exposed to it the lustre of the silver is replaced by a tarnish of silver oxide. If litmus, indigo, and other colouring matters are brought into contact with it, they are rapidly bleached. Again, a delicate test for ozone is moist starch paper containing some potassium iodide, for the iodine is freed from the potassium iodide by the ozone and at once makes the starch blue. There is a popular opinion that ozone is found in considerable quantities in the air of certain localities, and that such air is particularly healthful; but there is much doubt as to whether any ozone is found in air, and as to its powers of invigoration absolutely nothing is known.

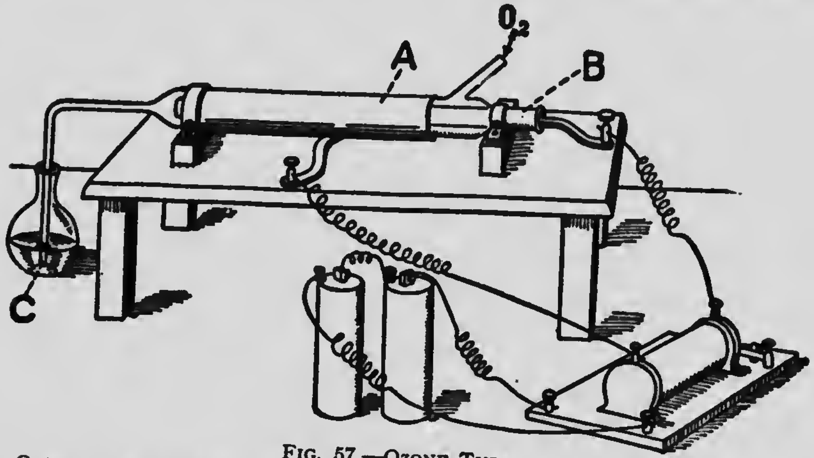

FIG. 57.—OZONE TUBE

A. Outer tube with metallic coating. B. Inner tube with metallic coating. C. Flask containing a solution of potassium iodide. O. Tube through which the oxygen enters.

As ozone attacks organic matter it is a valuable disinfectant; in fact, it is now used commercially to purify air and water; and as cheaper methods of preparation are learned, it will probably be used very extensively for such purposes.

241. Hydrogen peroxide. — Hydrogen peroxide is most readily prepared by acting on barium peroxide with dilute sulphuric acid:

$$BaO_2+H_2SO_4 \longrightarrow H_2O_2+BaSO_4.$$

It is generally used in the form of a dilute solution. The pure peroxide, a syrupy liquid, if dropped on the hand, produces a blister. When heated it decomposes into water and oxygen. Diluted with water it is moderately stable but, if slightly acidified, it can be kept for a long time.

It is, like ozone, a powerful oxidizing agent. For example, it converts lead sulphide into lead sulphate. Indeed, on account of this property it is used to restore the colour to old pictures, in which the lead carbonate has become converted into lead sulphide owing to the sulphurous gases in the air. Again, like ozone it liberates iodine from a solution of potassium iodide. On account of its oxidizing power it is also an effective bleaching material, and is more and more replacing sulphurous acid for this purpose, as its effect is more permanent than that of the latter substance. Accordingly, it is much used commercially for bleaching wool, silk, straw, and wood, and some women use it for bleaching their hair. On account of its oxidizing property it is a powerful antiseptic, and is used medicinally as a wash and a gargle.

It is rather remarkable that hydrogen peroxide is also sometimes a powerful reducing agent. In reducing, however, it is itself reduced to water. For example, it reduces silver oxide to silver according to the following equation:

$$Ag_2O+H_2O_2 \longrightarrow 2Ag+H_2O+O_2.$$

242. Test for hydrogen peroxide.—The tests that are used for ozone usually give the same reaction with hydrogen peroxide. Iodized starch paste is a very sensitive test for both, but does not distinguish between them. The oxidizing of silver is a rough test for ozone, which distinguishes it from hydrogen peroxide.

QUESTION

1. Name three important bleaching substances; state how each acts chemically in bleaching, and what materials are best bleached by each.

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(References are to pages. The number of a page printed in black-face type indicates that there is an illustration on that page.)

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Data regarding Elements mentioned in this Volume

NAME	Symbol	Approximate Atomic Weight	Valency
Aluminium	Al	27	III
Antimony	Sb	120	III, V
Argon	A	40	0
Arsenic	As	75	III, V
Barium	Ba	137	II
Bromine	Br	80	I
Cæsium	Cs	133	I
Calcium	Ca	40	II
Carbon	C	12	IV
Chlorine	Cl	35.5	I
Copper	Cu	63.6	I, II
Fluorine	F	19	I
Gold	Au	197	I, III
Helium	He	4	0
Hydrogen	H	1	I
Iodine	I	127	I
Iron	Fe	56	II, III
Krypton	Kr	83	0
Lead	Pb	207	II
Lithium	Li	7	I
Magnesium	Mg	24	II
Manganese	Mn	55	II, IV
Mercury	Hg	200	I, II
Neon	Ne	20	0
Nickel	Ni	58.7	II
Niton	Nt	222.4	0
Nitrogen	N	14	III, V
Oxygen	O	16	II
Phosphorus	P	31	III, V
Platinum	Pt	195	IV
Potassium	K	39	I
Radium	Ra	226	II
Silver	Ag	108	I
Sodium	Na	23	I
Strontium	Sr	87.6	II
Sulphur	S	32	II, IV, VI
Tin	Sn	119	II, IV
Xenon	Xe	130	0
Zinc	Zn	65	II

Table of Solubilities

	Aluminium	Ammonium	Antimony	Arsenious	Barium	Calcium	Copper	Ferrous	Ferric	Lead	Magnesium	Manganese	Mercurous	Mercuric	Potassium	Sodium	Silver	Zinc
Bromide....	S	S	Ss	S	S	S	S	S	S	Ss	S	S	I	S	S	S	I	S
Carbonate..	....	S	....	....	I	I	I	I	....	I	I	I	I	I	S	S	I	I
Chlorate....	S	S	....	....	S	S	S	....	....	S	S	....	S	S	S	S	S	S
Chloride....	S	S	Ss	S	S	S	S	S	S	Ss	S	S	I	S	S	S	I	S
Hydroxide..	I	S	Ss	S	S	Ss	I	I	I	I	I	I	....	I	S	S	....	I
Iodide.....	S	S	Ss	Ss	Ss	S	....	S	....	I	S	S	I	I	S	S	I	S
Nitrate.....	S	S	....	....	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Oxide......	I	....	Ss	S	I	Ss	I	I	I	I	I	I	I	I	S	S	I	I
Phosphate..	I	S	....	....	I	I	I	I	I	I	I	Ss	I	I	S	S	I	I
Sulphate...	S	S	....	....	I	Ss	S	S	S	I	S	S	Ss	S	S	S	Ss	S
Sulphide....	....	S	I	I	S	Ss	I	Ss	....	I	S	I	I	I	S	S	I	I
Sulphite....	....	S	....	....	I	Ss	S	Ss	....	I	Ss	....	....	....	S	S	S	Ss

S=Soluble in water. I=Insoluble in water. Ss=Slightly soluble in water.