ANTOINE LAURENT LAVOISIER (1743-1794)

Founder of modern chemistry. The cut is from a picture of a monument erected in his honor in Paris. Just back of it are seen the pillars of the church of St. Mary Magdalene. The erection of this church was begun in 1806 by Napoleon I, in commemoration of his victories

FIRST COURSE IN CHEMISTRY

BY

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AND

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GINN AND COMPANY, BOSTON
NEW YORK · CHICAGO · LONDON
ATLANTA · DALLAS · COLUMBUS · SAN FRANCISCO

315.3

The Athenæum Press
GINN AND COMPANY · PROPRIETORS · BOSTON · U.S.A.

PREFACE

In preparing this introduction to the science of chemistry the authors have endeavored to provide a text easily within the grasp of the average high-school student. Their effort has been to make the subject interesting, to use simple language, to develop the theoretical portions briefly and as a natural outcome of facts already presented, and to emphasize as much as possible the applications of chemistry in everyday life. The authors realize that the great majority of the students of chemistry in our secondary schools will never go further in the formal study of the science, and the book is primarily for them. It will be found, however, that the requirements of the College Entrance Examination Board have been fully met.

In addition to the applications to metallurgy and to manufacturing which are always of interest, an unusual amount of matter relating to agriculture, to household chemistry, and to sanitation has been introduced. Since the compounds of carbon play so important a part in our daily life, their discussion has been made more ample than is usual in an elementary course, and the chapters devoted to these compounds have been brought into their proper place in the text.

While thus emphasizing in every legitimate way the applications of chemistry, the authors have never lost sight of the fact that they are introducing young minds to the elements of a wonderful science and that it is due both to the student and to the science to exercise care in diction, candor in spirit, moderation in statement, and logic in presentation. It would not be a difficult task to write a more interesting book of popular chemical information — a sort of wonder-book of unconnected facts; but the authors feel that all students, particularly those who do not expect to continue their work in college, should have some just impression of the spirit of a science and of scientific thought as well as of the contributions of the science to human comfort. Some responsibility for vivacity, for interesting bits of collateral information, and, especially, for stimulating interest in the practical applications of chemistry as illustrated in local industries must always rest upon the teacher.

Directions for laboratory work will be found in a separate volume entitled "Exercises in Chemistry." While these exercises have been chosen primarily to demonstrate the principles developed in the textbook, great care has been exercised to reduce the requirements for apparatus and the cost of chemicals to a minimum. In the Appendix will be found some suggestions in regard to theme writing. The authors are convinced that many advantages will be gained by following up these suggestions.

A great deal of labor has been expended in securing the illustrations for the text, and it is believed that these will add much to the interest of the book and to the clearness of the presentation. The authors gratefully acknowledge their indebtedness to a number of their colleagues, especially to James R. Withrow and John F. Lyman, and to Robert C. Hummell, who has been kind enough to read the proof sheets. They are also under obligations to many other individuals and to manufacturing firms and wish to mention especially the following: Charles Hoover, in charge of the water-filtration plant, and Clarence Hoover, in charge of the sewage-disposal plant, Columbus, Ohio; Donald G. Kohr of the Lowe Brothers Paint Co.; Frank O. Clements of the National Cash Register Co.; Dr. C. H. Viol of the Standard Chemical Co.; Dr. H. P. Armsby, Pennsylvania State College; R. E. Humphrey, chief chemist, Standard Oil Co.; The Pittsburgh Plate Glass Co.; The H. L. Dixon Co.; The American Steel and Wire Co.; The Hydraulic Press Manufacturing Co.; The German Kali Works; The Chili Niter Co.; The Picher Lead Co.; The United States Beet Sugar Industry; The Keever Starch Co.; The Lackawanna Steel Co.; The American Rolling Mills Co.

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FIRST COURSE IN CHEMISTRY

CHAPTER I

BURNING

Introduction. Very few of us can watch a fire raging without mingled feelings of wonder and awe. We are impressed by the evidence it presents of uncontrolled forces at work; we are conscious of a sense of mystery as to what becomes of the things that have been consumed; we wonder about the cause of the spectacle. We are not surprised that in earlier ages fire and other similar occurrences — lightning, volcanic eruptions, the aurora of northern skies — should have inspired worship, awakened fear, aroused curiosity, and at length led to patient and laborious study.

That the explanation of burning is by no means a simple matter is shown by the fact that, notwithstanding all the study which had been devoted to it, it was not until about the time that our national war for independence was being fought, less than a century and a half ago, that the fundamental facts of combustion were recognized. It will be instructive to follow a few experiments attentively and see what these facts are.

A burning candle. Two facts about a burning candle are at once apparent: (1) the material of which the candle is composed disappears; and (2) heat and light are given out in the process. If a dry wide-mouthed bottle is inverted over the flame (Fig. 1), a further fact can be learned: as the candle burns, moisture is deposited upon the cold inside walls of the bottle. Furthermore, if the bottle is removed from over the flame and a little clear limewater at once poured into it and gently shaken, the clear liquid becomes milky, whereas it does not do this to any considerable extent if the bottle has not been held over the flame. It is therefore evident that, in burning, the candle is not really destroyed, but from it are formed water and another substance which renders clear limewater milky. This latter substance is a gas and is known as carbon dioxide or carbonic acid gas.

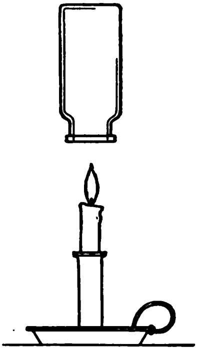

FIG. 1. Collecting the products formed from a burning candle

Increase in weight during burning. If the experiment is repeated under the conditions represented in Fig. 2, an additional fact may be learned. The candle *A* is placed on one pan of the balance. Over it is suspended a wide glass tube *B* (a lamp chimney serves very well) loosely filled with pieces of quicklime or caustic potash, both of which substances have been found to absorb moisture and also carbon dioxide. The whole apparatus is carefully counterpoised by weights *C*; then the candle is lighted. As the candle burns, the pan upon which it rests gradually sinks, indicating that the gases formed during burning and

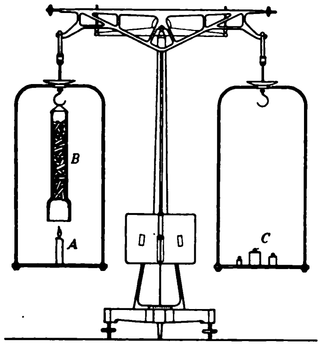

FIG. 2. Increase in weight during burning

absorbed in the tube over the flame are heavier than the part of the candle which has burned.

The burning of iron. Some additional information may be obtained by burning iron. Two or three grams of fine iron powder is placed in a small evaporating dish and accurately weighed. The dish containing the iron is then strongly heated by a laboratory lamp (known as a Bunsen burner), as shown in Fig. 3. As the heating proceeds, no fumes or gases can be discovered, but the iron glows and turns into a dark-red powder which in no way resembles the original iron. If the crucible and contents are now cooled and weighed again, they will be found to weigh more than before the iron was burned. Other metals, such as lead, tin, and zinc, act in a similar way, the product formed, or the *ash*, always being heavier than the unburned metal.

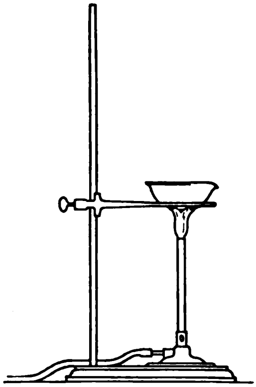

FIG. 3. The burning of iron

This increase in weight is one of the most striking facts of burning. Unless we assume that weight has been created out of nothing (which is contrary to all our experience), we must suppose that substances, in burning, withdraw from the air something possessing weight. This suggestion can be put to a test at once.

The burning of phosphorus. A piece of phosphorus the size of a pea is placed upon a crucible lid supported on a flat cork floating in a trough of water (Fig. 4). The phosphorus is set on fire by touching it with a lighted match, and a good-sized bottle or bell jar is inverted over it, as is shown in the figure. At first a few bubbles of air are forced out, owing to the expansion of the air occasioned by the heat. Then the water rises in the bell jar, showing that air is being used up. Soon the phosphorus ceases to burn, although there is plenty of air left. Very careful experiments show that burning will continue until about one fifth of the air has been used up, and will then cease. The smoke of the burning phosphorus gradually disappears, owing to the fact that it has dissolved in the water.

This experiment suggests that some material, constituting about one fifth of the air by volume, is withdrawn from the air by a burning substance such as phosphorus.

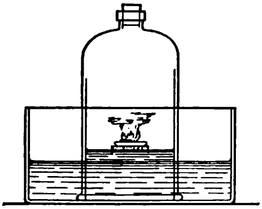

FIG. 4. The burning of phosphorus

Experiment of Priestley. The clue to the nature of the material withdrawn from the air was first found by Joseph Priestley, an Englishman, in 1774. He obtained a red solid (which was then called red precipitate of mercury, but which is merely the ash of mercury burned in the air) and heated it strongly in a closed tube. He found that a remarkable gas (or air, as he called it) was given off, in which a candle burned much more brilliantly than in ordinary air, while mercury was left in the tube. The experiment may be repeated as is shown in Fig. 5, introducing a splinter of wood with a glowing spark on the end into the tube in which the red precipitate is being heated. The spark at once bursts into a flame. It was later shown that phosphorus will use up *all* of this air

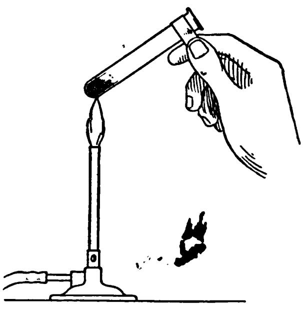

FIG. 5. Heating the ash of mercury

in burning. Priestley did not realize the importance of his experiment, but its significance was quickly understood by the French chemist Lavoisier (see frontispiece).

Experiment of Lavoisier. Lavoisier believed that air is in part composed of this gas, which he named *oxygen*, and that, in burning, substances combine with oxygen. To test this idea he devised the following experiment:

Details of Lavoisier's experiment. A weighed quantity of pure mercury was placed in a retort *A* (Fig. 6), which communicated with a bell jar *B* containing air confined over mercury in *C*. The retort and its contents were heated by the furnace *D* for twelve days just below the boiling point of mercury, and it was found that a part of the mercury had been burned, forming a red ash, and that from 7 to 8 cu. in. of air had been absorbed during the process. The red ash was collected and placed in a small retort arranged in such a way that any gas given off from it could be collected and measured. It was then strongly heated, by which process the mercury was recovered and a gas collected. In quantity this proved to be equal to from 7 to 8 cu. in., or the same volume that had been previously absorbed. It was not ordinary air, however, but *oxygen*. In this way a definite quantity of mercury was first burned in air, and the ash formed was then decomposed into mercury and oxygen.

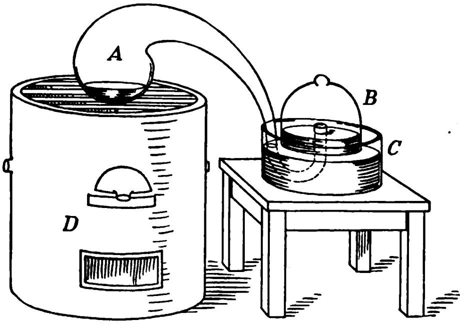

Fig. 6. Apparatus used by Lavoisier to prove that mercury absorbs oxygen during burning

Conclusions. These experiments, together with many later and much more accurate ones, have demonstrated that burning is really a union between the material burned and the oxygen which is present in the air, and that the total weight of the material burned plus that of the oxygen used up equals the weight of the products formed. It will be seen that the discovery of oxygen and the demonstration of the real nature of burning were greatly aided by the happy chance that when the ash of mercury is strongly heated, the act of burning is turned around, or *reversed*, oxygen and mercury being recovered. This fact may be represented in an equation as follows:

$$\text{mercury ash} \rightleftarrows \text{mercury} + \text{oxygen}$$

The double arrows indicate that the change may take place in either direction, according to the conditions.

Additional questions. This still leaves many questions unanswered. What causes the combustion to take place? Why will some things burn and others not? Where do the heat and light come from, and what finally becomes of them? In part these questions will be answered as we go along.

The phlogiston theory of burning. The reason why Priestley failed to understand the part which oxygen plays in burning was that he shared the prevailing views of his time and could not easily give up the ideas he had always held. For a century and a half burning had been regarded as occasioned by the escape of an invisible material known as *phlogiston.* Doubtless this idea was suggested by the puffing and sputtering of materials while they burn. It was thought that when mercury burns, a constituent of it, namely, phlogiston, escapes, so that the ash formed is equal to the mercury minus phlogiston. To recover the mercury from the ash, phlogiston must be restored to it, and it was hard to see how merely heating it could do this. Priestley thought that the oxygen given off must be air from which phlogiston had been extracted and returned to the mercury, and he called it dephlogisticated air. Evidently this theory could not explain why metals get heavier as they burn, and when oxygen was discovered, the theory of phlogiston was soon abandoned.

EXERCISES

1. How do the ashes of coal compare in weight with the original coal? Can you suggest a reason why some coals, when burned, leave more ashes than others?

2. How do you account for the fact that when a lamp is lighted, a film of moisture is deposited on the chimney? Is the film deposited on the inside or on the outside of the chimney? Why does the film soon disappear?

3. Could you improve the details of the apparatus illustrated in Fig. 4 so that no air would be forced out?

4. How accurately does Lavoisier seem to have measured his gases? What is the percentage error? Do you think his conclusions from such experiments were justified?

5. How did the fact that the burning of mercury is reversible aid in the discovery of oxygen?

6. In Fig. 6 how would it be known that air had been absorbed?

7. It was known to the phlogistonists that things would not burn in the absence of air. Was this in accord with their theory?

8. What is the derivation of the word *phlogiston* (see dictionary)?

Topics for Themes*

Lavoisier (Thorpe, Essays in Historical Chemistry).

Phlogiston (see encyclopedia).

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* Refer to Appendix for suggestions in connection with topics for themes.

CHAPTER II

ELEMENTS AND COMPOUNDS

Elements. Having found that by merely heating the ash of mercury (or *mercuric oxide*, as it is now called) two entirely different materials, mercury and oxygen, are obtained from it, the inquiry naturally arises: Can still other substances be obtained by heating either of these two? Will any agency other than heat bring about their decomposition? Many efforts to decompose these substances have been made, but none have succeeded. On this account they are called *elementary substances* or *elements.*

It is not always easy to prove that a given substance is really an element. Some way as yet untried may be successful in decomposing it into other simpler forms of matter. Water, lime, and many other familiar substances were at one time thought to be elements, but are now known to contain two or more elements.

Compounds. Substances such as mercuric oxide, which are formed by the union of two or more elements, are called *compounds.* Experiments have shown that any given compound is always made up of the same elements and that it has a *perfectly definite percentage* of each one; for example, mercuric oxide is always composed of mercury and oxygen combined in the proportion 92.6 per cent mercury and 7.4 per cent oxygen. We shall learn of other characteristics of compounds as we proceed.

As a rule the appearance of a compound offers no suggestion as to what elements are present in it. Thus, the red solid, mercuric oxide, is formed by the union of the silvery liquid, mercury, with the invisible gas, oxygen. The familiar colorless liquid, water, is formed by the union of two invisible gases, oxygen and hydrogen.

Chemical changes; chemical action. Such changes as those taking place in the conversion of mercuric oxide into mercury and oxygen or in the burning of any substance are called *chemical changes*, and in describing them we say that *chemical action* has taken place. In all such changes the substances resulting from the chemical action differ in composition from the substances originally present, and usually differ from them in appearance as well. We shall see later on that there are other important changes which always accompany chemical action.

Chemical affinity. The force that causes elements to unite and holds them in combination in compounds is called *chemical affinity*. We know very little about the nature of this force, just as we know very little about the force of gravitation. It is evident, however, that there is such a force, and it is convenient to have a name by which we can refer to it.

Number of elements. The number of substances now considered to be elements is not large — about eighty in all. Many of these are rare, and very few of them form any large fraction of the materials in the earth's crust. Clarke gives the following estimate of the composition of the solid portion of the earth's crust:

COMPOSITION OF THE EARTH'S CRUST

Oxygen	47.07%	Magnesium	2.40%
Silicon	28.06%	Sodium	2.43%
Aluminium	7.90%	Potassium	2.45%
Iron	4.43%	Hydrogen	0.22%
Calcium	3.44%	Other elements	1.60%

A complete list of the elements is given on the back cover page. In this list the more common of the elements are printed in heavier type. It is not necessary to study more than one third of the total number of elements to gain a very good knowledge of chemistry.

Elements in the human body. Comparatively few of the elements appear to be essential to life. The following table, compiled by Sherman, gives the average composition of the human body. So far as we can judge, these are the only ones upon which living organisms are dependent, though traces of others may be necessary.

AVERAGE COMPOSITION OF THE HUMAN BODY

Oxygen	65.00%	Phosphorus	1.00%	Magnesium	0.05%
Carbon	18.00%	Potassium	0.35%	Iron	0.004%
Hydrogen	10.00%	Sulfur	0.25%	Iodine	traces
Nitrogen	3.00%	Sodium	0.15%	Fluorine	traces
Calcium	2.00%	Chlorine	0.15%	Silicon	traces

Occurrence of the elements. Most of the elements occur in nature not as uncombined substances, but in the form of chemical compounds. When an element does occur uncombined, as is the case with gold and sulfur, we say that it occurs *in the free state* or *native*; when it is combined with other substances in the form of compounds, we say that it occurs *in the combined state*, or *in combination.*

Names of elements. The names given to the elements have been selected in a great many different ways. Some names, such as iron and gold, are very old, and their original meaning is obscure. Many names indicate some striking property of the element. The name *bromine*, for example, means "stench," referring to the extremely unpleasant odor of the substance. Other elements are named from countries or localities, as germanium and scandium.

Symbols. In indicating the elements, chemists have adopted a system of abbreviations. These are known as *symbols*, each element having a distinctive symbol. Sometimes the initial letter of the name is adopted to indicate the element. Thus, I stands for iodine, C for carbon. Usually it is necessary to add some other characteristic letter to the symbol, since several names may begin with the same letter. Thus, C stands for carbon, Cl for chlorine, Cd for cadmium. Sometimes the symbol is an abbreviation of the name in some other language. In this way Fe (Latin, *ferrum*) indicates iron. The symbols will be found in the list of elements given on the back cover page. They will become familiar through constant use.

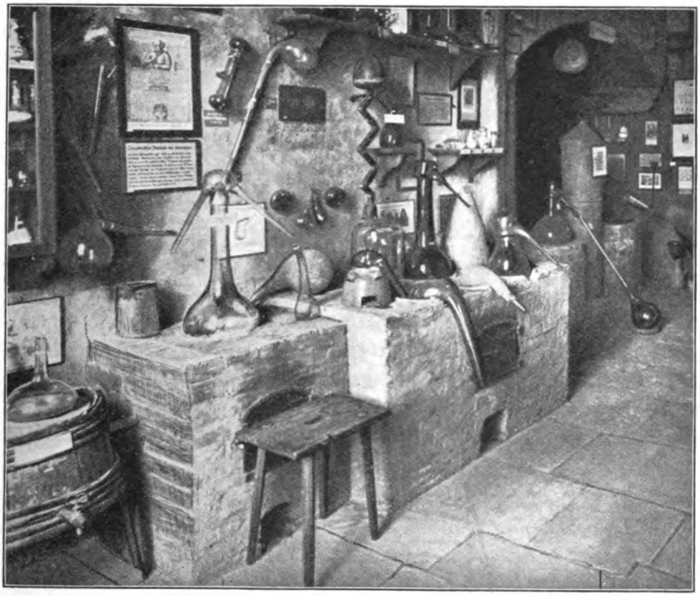


FIG. 7. An alchemist's laboratory, in the Deutsches Museum, Munich

The number of compounds. The number of compounds which have been described and which can be made when desired is very large, and each year many more are added to the list. About 200,000 are known that contain the element carbon as one constituent, and the total number listed in the large handbooks of chemistry is much larger. Fortunately it is not necessary to become familiar with any large number of these in order to gain an understanding of the principles of chemistry.

Alchemy. In olden times it was thought that some way could be found to change one element into another, and a great many experiments were made to accomplish this transformation. Most of these efforts were directed toward changing the commoner metals into gold, and many fanciful ways for doing this were described. The chemists of that time were called *alchemists*, and the art which they practiced was called *alchemy*. Failing to accomplish this transformation, the alchemists gradually became convinced that the only way in which common metals could be changed into gold was by the wonderful power of a magic substance which they called the *philosopher's stone*, which would accomplish this transformation by its mere touch and would in addition give perpetual youth to its fortunate possessor. No one has ever found such a stone, but one of the most brilliant discoveries of modern times has demonstrated that at least some of the elements are of their own accord very slowly changing into others.

EXERCISES

1. What other means of decomposing a compound can you suggest, aside from heating?

2. How would you define a compound? an element?

3. What is meant by the earth's crust?

4. Does the fact that a substance undergoes no change on heating show it to be an element?

5. Read over the list of elements. What ones do you know to occur native?

6. Aluminium is much more abundant than iron (see table). How do you account for the much greater cheapness of iron?

7. Consult the dictionary for the derivation and significance of the following names: *phosphorus*, *hydrogen*, *germanium*, *columbium*, *chlorine*, *argon*, *copper*, *selenium*, *thorium*.

8. How would you define (*a*) chemical changes and (*b*) chemical action?

9. What weight of oxygen is present in 500 g. of mercuric oxide? *Ans.* 37 g.

TOPICS FOR THEMES

Methods of naming the elements, with examples to illustrate (see dictionary).

The philosopher's stone and the elixir of life (see encyclopedia).

The alchemists (Muir, The Story of Alchemy; Bird, Modern Science Reader).

CHAPTER III

OXYGEN

Introduction. Having become acquainted with a few of the characteristics of the class of substances called elements, we shall now turn to a more detailed study of two members of this class, namely, oxygen and hydrogen. It is natural that we should begin with oxygen, since it is the most abundant of all elements, occurs in nature in great quantities in the elementary state, and plays such an important part in the familiar processes of burning and breathing.

Discovery. Priestley's experiment (1774) of heating mercuric oxide (p. 4) is looked upon as constituting the discovery of oxygen, though it is now known that the Swedish chemist, Scheele, had prepared it some years earlier by heating niter. An account of this latter experiment was not published until 1777, while Priestley at once made known the results of his experiment.

The name *oxygen*. The name *oxygen*, suggested by Lavoisier, means "acid producer," for he thought that the class of substances known as acids owe their characteristic properties to the presence in them of this element. We now know that there are acids which contain no oxygen.

Occurrence. Oxygen is by far the most abundant of the elements. In the free state it forms a considerable part of the atmosphere, 100 volumes of *dry* air containing about 21 volumes of oxygen. Combined with other elements, it forms eight ninths of water, nearly one half of the rocks constituting the earth's crust, and over one half of animal and vegetable organisms; for example, 65 per cent by weight of the human body is oxygen.

Preparation. Among the great number of compounds containing oxygen there are a few which can be decomposed easily in such a way as to set the oxygen free.

1. ***Preparation from mercuric oxide.*** Mercuric oxide has been found to consist of 7.4 per cent oxygen and 92.6 per cent mercury. If a small quantity of the red powder is placed in a narrow test tube and heated in a Bunsen flame (Fig. 5), it is rapidly decomposed into its constituent elements. The mercury is seen to deposit on the sides of the tube, while the presence of oxygen is shown by the fact that a glowing spark on the end of a splinter of wood inserted into the tube bursts into a bright flame. The method is of interest because of its simplicity and because it first led to the discovery of oxygen. It is too expensive to serve as a laboratory method.

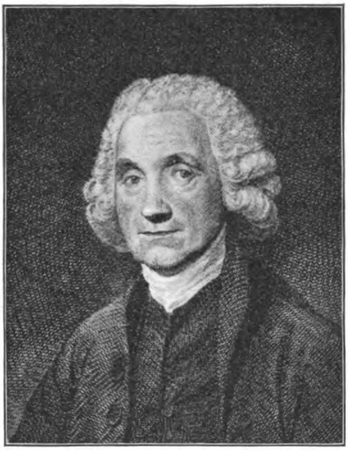


FIG. 8. Joseph Priestley (1733–1804)
The discoverer of oxygen

2. ***Preparation from potassium chlorate*** (*usual laboratory method*). Potassium chlorate is a white solid which has been found to consist of 31.9 per cent potassium, 28.9 per cent chlorine, and 39.2 per cent oxygen. When this material is heated above its melting point, the oxygen is given off,

leaving a compound of chlorine and potassium called potassium chloride. The changes may be represented as follows:

$$\underset{\begin{bmatrix}\text{potassium}\\ \text{chlorine}\\ \text{oxygen}\end{bmatrix}}{\text{potassium chlorate}} \longrightarrow \underset{\begin{bmatrix}\text{potassium}\\ \text{chlorine}\end{bmatrix}}{\text{potassium chloride}} + \text{oxygen}$$

The evolution of the oxygen begins at about 400°. It has been found, however, that if a small quantity of certain finely powdered solids, such as manganese dioxide, is mixed with the potassium chlorate, not only is the oxygen given off more uniformly, but the rate at which it is evolved at any given temperature is greatly increased. Just how the manganese dioxide brings about this result is not definitely known. The amount of oxygen obtained from a given weight of potassium chlorate is just the same whether the manganese dioxide is present or not, and just as much of the dioxide remains at the end as was added. As we shall see, this kind of action is not at all uncommon.

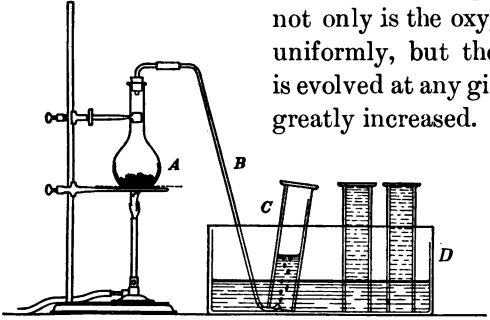


Fig. 9. The preparation of oxygen from potassium chlorate

Directions for preparing oxygen. A convenient way of preparing oxygen from potassium chlorate is illustrated in the accompanying diagram (Fig. 9). A mixture consisting of four parts of potassium chlorate and one part of manganese dioxide is placed in the flask *A* and gently heated. The oxygen is evolved and escapes through the tube *B*. It is collected by bringing over the end of the delivery tube the mouth of a bottle or cylinder *C* completely filled with water and inverted in a vessel of water as shown in the figure. The gas rises in the bottle and displaces the water.

The collection of gases. The method just described for collecting oxygen illustrates the general way in which gases are transferred from one vessel to another when they are insoluble in water or nearly so. The vessel *D* (Fig. 9), containing the water in which the bottles are inverted, is called a *pneumatic trough.* Gases which are soluble in water may be collected in a similar way over mercury.

3. ***Commercial preparation of oxygen.*** When oxygen is prepared for commercial purposes, it is usually obtained either from water or from air. As we shall soon see, water contains 88.81 per cent of oxygen and 11.19 per cent of hydrogen. It is not practicable to decompose it into its elements by heat, but the decomposition is easily effected by the use of electrical energy. The method may be illustrated by the following laboratory experiment:

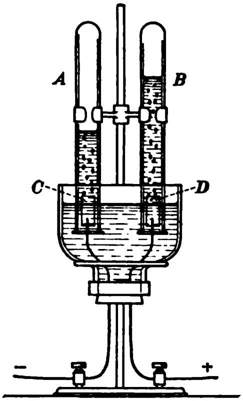


FIG. 10. The decomposition of water into oxygen and hydrogen by the electric current

Two tubes, *A* and *B* (Fig. 10), are filled with water and inverted in a vessel of water to which a little sulfuric acid has been added. A piece of platinum foil, *C* and *D*, attached to a wire is then brought under the end of each tube. When these wires are connected with a suitable source of current, supplying from 6 to 10 volts (about 6 dichromate cells in series), bubbles of gas will be seen to collect in each tube. These gases are oxygen and hydrogen. The volume of the hydrogen liberated is twice that of the oxygen. The reasons for adding sulfuric acid will be explained later on.

This process, carried out on a large scale, serves as a commercial method for preparing oxygen and hydrogen as well. Oxygen is also obtained commercially from air, as will be described later (p. 93). The gas so prepared is pumped into steel tubes (Fig. 11) and is sold in this form.

Laboratory methods and commercial methods. As we go along we shall see that the methods used in making various substances in the laboratory are usually different from those employed commercially. In the laboratory, where relatively small quantities are desired, the easiest or most instructive way is preferred. In commerce, economy is the deciding factor. Moreover, it often happens that a method which will not work well on a small scale works admirably with commercial quantities, or that the value of a second product (*by-product*) obtained at the same time makes a method a success.

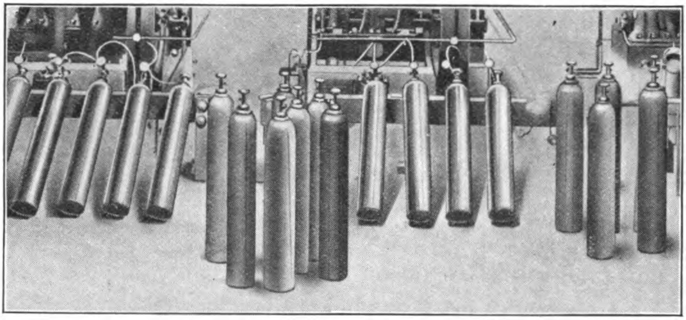


FIG. 11. Oxygen ready for the market

Properties of a substance. By the properties of a substance we mean all of those characteristics, or marks, by which we recognize it. Some of these are concerned with the way the substance affects us, such as taste, odor, color, and luster. Others are measurable quantities, such as density, hardness, solubility, boiling point, and freezing point.

Properties of oxygen. If we make a study of the properties of oxygen, we find that it is a colorless, tasteless, odorless gas slightly heavier than air. At a temperature of 0° and under a pressure of 1 atmosphere, 1 liter of it weighs 1.4290 g., while under the same conditions 1 liter of air weighs 1.2928 g. It is but slightly soluble in water. Like other gases, oxygen may be liquefied by applying sufficient pressure to the very cold gas. This liquid is pale blue in color. It boils at – 182.9° and freezes to a snowlike solid at – 235°.

Chemical conduct. In addition to the properties of a substance we always wish to know how it conducts itself toward a number of other familiar substances, and we speak of this as the *chemical conduct* of the substance.

At ordinary temperatures oxygen is not very active. Most substances are either not affected at all by it or the action is so slow as to escape notice. At higher temperatures, however, it is very active and unites directly with most of the elements. This may be shown by heating various substances until they are just ignited in air, and then bringing them into vessels containing oxygen, when they burn with greatly increased brilliancy. Thus, a glowing splint introduced into a jar of oxygen bursts into flame. Sulfur burns in air with a very weak flame and feeble light; in oxygen the flame is increased in size and brightness (Fig. 12). Substances which burn readily in the air, such as phosphorus, burn in oxygen with dazzling brilliancy. Even substances which burn in the air with great difficulty, such as iron, burn readily in oxygen.

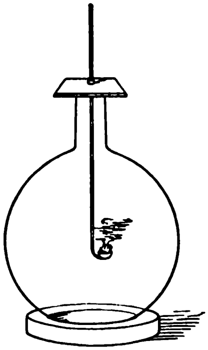


FIG. 12. Burning sulfur in oxygen

Oxidation. We have seen that the burning of an element in the air is really its union with oxygen. Many compounds as well as elements burn readily both in air and in oxygen; among these are coal, wood, oil, and gas. In the majority of such cases the compound is completely decomposed and each of its constituent elements combines with oxygen. Thus, most oils are made up of carbon and hydrogen, and when the oil burns it is converted into a compound of carbon and oxygen (carbon dioxide) and another of hydrogen and oxygen (water). Less frequently the compound undergoes no decomposition but merely as a whole combines with oxygen. All of these actions are called *oxidation.* We shall see later that still other kinds of chemical action are called oxidation.

Oxides. Any compound consisting of oxygen and some one other element is called an *oxide.* Thus, burned iron is iron oxide; burned mercury is mercury oxide; burned oil yields carbon dioxide and hydrogen oxide (water). When more than one element, aside from oxygen, is present in a compound, it is not called an oxide, but some other name is given it.

Many of the oxides are familiar substances. Thus, water is oxide of hydrogen and lime is oxide of calcium. All but about half a dozen elements form oxides, and many of them form more than one, so that a large number of these compounds is known. Some of them are solid bodies, as in the case of the oxides of mercury, iron, and phosphorus; others are liquids, of which class water is the most familiar example; quite a number are gases, as is true of the oxide of carbon and of sulfur.

Combustion. Sometimes oxidation takes place so slowly that no light is seen, and unless careful measurements are made, no heat is noticed. The decay of vegetable matter such as wood and leaves, is an example of this slow oxidation. In other cases, as with burning phosphorus or iron, light is given off either as a flame or as a glow called *incandescence.* Oxidation accompanied by light is called *combustion.*

Heat of oxidation and combustion. Evidently a given substance may either undergo a slow oxidation or it may undergo combustion. Thus, a piece of phosphorus, exposed to the air in a cold room, slowly wastes away until it has all disappeared into smoke consisting of an oxide of phosphorus; but if it is touched with a lighted match, it takes fire and burns very rapidly, giving out much heat in its combustion. The product is the same in both cases, namely, oxide of phosphorus. Apparently the difference lies in the amount of heat given off, but very accurate experiments demonstrate that this, too, is *exactly the same.* In the one case the action is so slow that the heat is conducted away as fast as it is liberated, and so it escapes notice; in the other it is given off so rapidly as to be very striking. A similar relation has been found to hold true in all cases of combustion. The heat given off is exactly the same whether the action is fast or slow, *provided the same compound is formed.*

Spontaneous combustion. It has been found that the rate at which oxidation goes on is greatly increased by raising the temperature of the material undergoing oxidation. Consequently, if the conditions surrounding oxidation are such that the heat given off cannot escape, the temperature will steadily rise, and because of this the rate of oxidation will increase. The increased heat thus set free will still further raise the temperature, until the oxidation passes into active combustion, the point at which this occurs being called the *kindling temperature.* Materials taking fire in this way are said to undergo *spontaneous combustion.* It will be seen that the essential conditions are (1) an existing slow oxidation and (2) good heat insulation. Linseed oil, used in paints, undergoes rather rapid oxidation in air, and oily rags left by painters not infrequently occasion disastrous fires. Fine, dry coal in the center of a heap or in the closed hold of a vessel sometimes takes fire. Almost any finely divided combustible material, such as sawdust or flour, is dangerous when stored in a warm, dry place. Sometimes the heat of fermentation, which is a kind of oxidation, will start a fire in a haystack or barn if the hay is not well dried before storing.

Importance of oxygen. Oxygen is one of the most important of the elements. It is essential to all forms of life except certain low forms of plant life. In the presence of certain minute microörganisms, which in some way assist in the process, the oxygen in the air acts upon the dead products of animal and vegetable life and converts them into harmless substances. In this way it acts as a purifying agent. For example, in sewage-disposal plants, sewage is forced into the atmosphere in fine sprays (Fig. 13), so that the oxygen can come in contact with the putrid matter in the sewage, thus purifying the sewage and preventing it

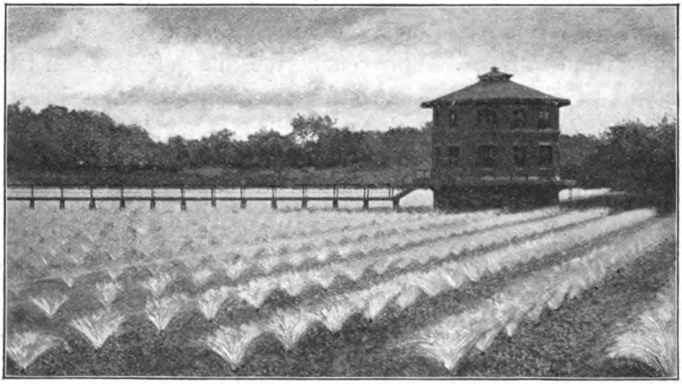


FIG. 13. Sewage-disposal plant, Columbus, Ohio, in which the sewage is sprayed into the air to secure its oxidation

from becoming a menace to health. The pure commercial oxygen is also used in the treatment of certain diseases and especially as a source of intense heat (see oxyhydrogen and oxyacetylene blowpipe).

EXERCISES

1. In Fig. 9, why does the water stay in the inverted cylinder? Why does the oxygen displace it? When a little oxygen has entered, why does not all the water run out?

2. What other liquids can you think of over which gases might be collected?

3. What does the word *pneumatic* mean (see dictionary)?

4. Can you find out what is the pressure of 1 atmosphere in pounds per square inch? in grams per square centimeter?

5. Since oxygen is such an active gas, why is it present in the atmosphere in such large quantities?

6. Can combustion take place without the emission of light?

7. Is the evolution of light always produced by combustion?

8. Why are oily rags more likely to start a fire than oil spilled on the floor?

9. From the percentages given (p. 15), what weight of potassium chlorate will be required to yield 10 g. of oxygen? *Ans.* 25.5 g.

10. What weight of mercuric oxide will be required to yield 10 g. of oxygen? *Ans.* 135.13 g.

11. Assuming the cost of potassium chlorate to be 50 cents per kilogram and that of mercuric oxide to be $1.50 per kilogram, what is the cost of the weight of each required in the preparation of 10 g. of oxygen? *Ans.* 1.27 cents and 20.27 cents.

TOPICS FOR THEMES

Joseph Priestley (Thorpe, Essays in Historical Chemistry).
Spontaneous combustion (see encyclopedia).

CHAPTER IV

HYDROGEN

Introduction. A great variety of materials undergo combustion, among them being coal, wood, oils, and various gases. One of these gases, hydrogen, is of special interest because it is an elementary substance.

Various combustible gases have been known from early ages, but they were long confused with each other. The gas hydrogen was first clearly recognized as a distinct substance by the English investigator, Cavendish, in 1776; he obtained it in pure condition and showed it to be different from all other known gases. It was named hydrogen by Lavoisier, the word meaning "producer of water."

Occurrence. Hydrogen occurs in the atmosphere in the free state, but only in traces. It occurs in enormous quantities in the atmosphere of the sun and certain other stars. In the combined state it is widely distributed, being a constituent of water as well as of all living organisms and of many of the products derived from them, such as wood, starch, and sugar. About 10 per cent of the human body is hydrogen. Combined with carbon it forms many compounds, which, mixed together, constitute petroleum and natural gas.

Preparation. Hydrogen can be prepared in a number of ways, three of which are of special interest:

1. ***By the action of metals on water.*** When brought into contact with certain metals under appropriate conditions, water gives up the whole or a part of its hydrogen, its

place being taken by the metal. In the case of a few of the metals this change occurs at ordinary temperatures. Thus, if a bit of the metal sodium is dropped on water, an action is seen to take place at once, sufficient heat being set free to melt the sodium, which runs about on the surface of the water. The change which takes place consists in the substitution of one half of the hydrogen of the water by the sodium, and may be represented as follows:

$$\text{sodium} + \underset{\begin{bmatrix}\text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{water}} \longrightarrow \text{hydrogen} + \underset{\begin{bmatrix}\text{sodium}\\ \text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{sodium hydroxide}}$$

The sodium hydroxide formed is a white solid which remains dissolved in the excess of undecomposed water and may be obtained by evaporating the solution to dryness. The hydrogen is evolved as a gas and may be collected by suitable means.

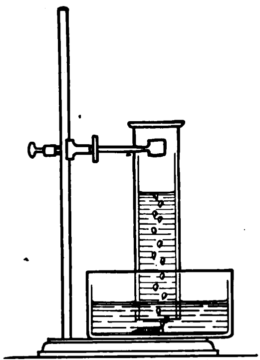


FIG. 14. The preparation of hydrogen by the action of sodium on water

Fig. 14 represents a simple form of apparatus used in preparing hydrogen by the action of sodium on water. Since the sodium is lighter than water, it is kept under the water by pushing a pellet of the metal into the end of a short piece of lead or tin pipe, the other end of which has been hammered until closed. The pipe containing the sodium is then dropped into a trough of water. Hydrogen is at once evolved and is collected by bringing over it a bottle or cylinder filled with water, as shown in the figure.

Other metals, such as magnesium and iron, decompose water rapidly but only at higher temperatures. When steam is passed over hot iron, for example, the iron combines with the oxygen of the steam, setting free all of the hydrogen. Experiments show that the change may be represented as follows:

$$\text{iron} + \underset{\begin{bmatrix}\text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{water}} \longrightarrow \text{hydrogen} + \underset{\begin{bmatrix}\text{iron}\\ \text{oxygen}\end{bmatrix}}{\text{iron oxide}}$$

The iron oxide formed is a reddish-black compound identical with that obtained by the combustion of iron in oxygen.

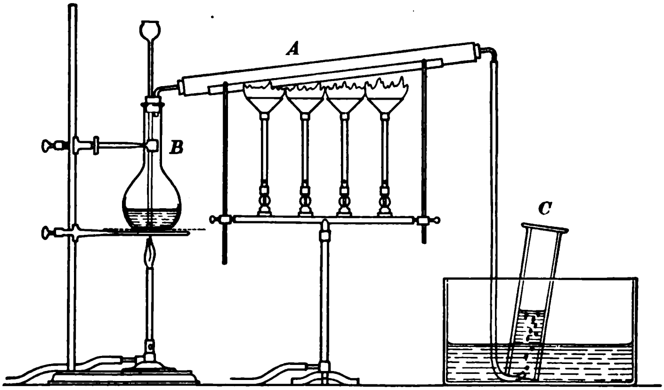


FIG. 15. The preparation of hydrogen by the action of iron on steam

Preparation of hydrogen from iron and steam. The apparatus used in the preparation of hydrogen from iron and steam is shown in Fig. 15. A porcelain or iron tube *A*, about 50 cm. in length and 2 cm. or 3 cm. in diameter, is partly filled with fine iron wire or tacks and connected as shown in the figure. The tube is heated slowly at first, until the iron is red-hot. Steam is then conducted through the tube by boiling the water in the flask *B*. The hot iron combines with the oxygen in the steam, setting free the hydrogen, which is collected over water in *C*.

2. ***By the action of metals on acids*** (*usual laboratory method*). In the laboratory, hydrogen is usually prepared from compounds known as acids, all of which contain

hydrogen. When acids are brought in contact with a number of the different metals, the latter dissolve and set free the hydrogen of the acid. It has been found most convenient and economical, in preparing hydrogen by this method, to use either zinc or iron as the metal and either hydrochloric or sulfuric acid as the acid. Hydrochloric acid is an aqueous solution of a gaseous compound known as hydrogen chloride (which consists of 2.77 per cent hydrogen and 97.23 per cent chlorine), while sulfuric acid is an aqueous solution of an oily liquid known as hydrogen sulfate (which consists of 2.05 per cent hydrogen, 32.70 per cent sulfur, and 65.25 per cent oxygen).

The changes taking place in the preparation of hydrogen from zinc and sulfuric acid may be represented as follows:

$$\text{zinc} + \underset{\begin{bmatrix}\text{hydrogen}\\ \text{sulfur}\\ \text{oxygen}\end{bmatrix}}{\text{sulfuric acid}} \longrightarrow \underset{\begin{bmatrix}\text{zinc}\\ \text{sulfur}\\ \text{oxygen}\end{bmatrix}}{\text{zinc sulfate}} + \text{hydrogen}$$

In other words, the zinc takes the place of the hydrogen in sulfuric acid. The resulting compound contains zinc, sulfur, and oxygen and is known as *zinc sulfate.* This remains dissolved in the water in the acid. It may be obtained in the form of a white solid by evaporating the liquid left after the metal has passed into solution.

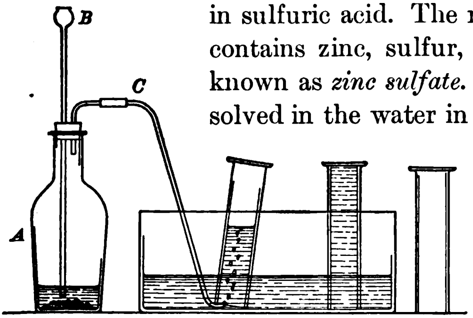


FIG. 16. The preparation of hydrogen by the action of metals on acids

Directions for preparing hydrogen from acids. The preparation of hydrogen from acids is carried out in the laboratory as follows: The metal is placed in a flask or wide-mouthed bottle

A (Fig. 16), and the acid is added slowly through the funnel tube *B*. The metal dissolves in the acid, while the hydrogen which is liberated escapes through the exit tube *C* and is collected over water. Pure sulfuric acid will not act readily upon pure zinc. The reaction may be started, however, by the addition of a few drops of a solution of copper sulfate.

3. ***Commercial preparation.*** In preparing hydrogen on a large scale for commercial uses the method of electrolysis of acidulated water is used, as explained on page 17.

Properties of hydrogen. Hydrogen resembles oxygen in that it is a colorless, tasteless, odorless gas. It is the lightest of all known substances, 1 liter of the gas weighing only 0.08987 g. Soap bubbles blown with hydrogen rapidly rise in the air.

Hydrogen is more difficult to liquefy than any other gas, with the exception of the rare gas helium. The English chemist, Dewar, however, in 1898 succeeded not only in obtaining hydrogen in liquid state but also as a solid. Liquid hydrogen is colorless. Its density, that is, the weight of 1 cc., is only 0.07. Its boiling point is $-252.7°$ and its melting point $-259°$. The solubility of hydrogen in water is very slight, being still less than that of oxygen.

Pure hydrogen produces no injurious results when inhaled. Of course one could not live in an atmosphere of the gas, since oxygen is essential to respiration.

Chemical conduct. At ordinary temperatures hydrogen is not an active element. Under suitable conditions, however, it combines with many of the elements, forming compounds known as *hydrides*. Thus, hydrogen and chlorine, when mixed together, will combine with explosive violence if heated or if exposed to the sunlight. The product formed in either case is called *hydrogen chloride*. Under suitable conditions hydrogen combines with nitrogen to form *ammonia*, and with sulfur to form the foul-smelling gas *hydrogen sulfide*. At ordinary temperatures hydrogen and oxygen may be mixed without action. If the mixture is heated to about 800°, or if a flame is brought in contact with it, a violent explosion takes place. Nevertheless, under proper conditions hydrogen may be made to burn quietly in either oxygen or air. The resulting hydrogen flame is almost colorless and is very hot. The combustion of the hydrogen is due to its union with oxygen and the product of the combustion is an oxide of hydrogen. That this compound is water may be easily shown by experiment.

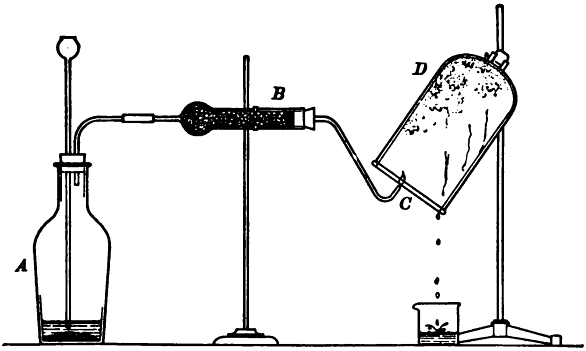


FIG. 17. Burning hydrogen and collecting the product of its combustion

Directions for burning hydrogen. The combustion of hydrogen in air may be carried out safely as follows: The hydrogen is generated in the bottle *A* (Fig. 17), is dried by conducting it through the tube *B* filled with some substance (usually calcium chloride) which has a great attraction for moisture, and escapes through the tube *C*, the end of which is drawn out to a jet. *When all the air has been expelled from the apparatus, the hydrogen may be ignited.* It then burns quietly, since only the small amount of it which escapes from the jet can come in contact with the oxygen of the air at any one time. By holding a cold, dry bell jar or bottle over the flame in the manner shown in the figure the steam formed by the combustion of the hydrogen is condensed, water collecting in drops on the sides of the jar.

Hydrogen does not support combustion. While hydrogen is readily combustible, it is not a supporter of combustion; in other words, substances will not burn in it. This may be shown by bringing a lighted candle supported by a stiff wire into a bottle or cylinder of the pure gas, as shown in Fig. 18. The hydrogen is ignited by the flame of the candle and burns at the mouth of the cylinder, where it comes in contact with the oxygen in the air. When the candle is thrust up into the gas, its flame is extinguished. If slowly withdrawn, the candle is relighted as it passes through the layer of burning hydrogen.

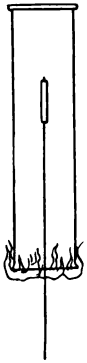


Fig. 18. Hydrogen extinguishes the flame of a candle

Reduction. On account of its tendency to combine with oxygen, hydrogen has the power of abstracting it from many of its compounds. Thus, if a stream of hydrogen generated in *A* (Fig. 19) and dried by passing through the tube *B* (filled with calcium chloride) is conducted through the tube *C*, which contains some copper oxide heated to a moderate temperature, the hydrogen abstracts the oxygen from the copper oxide. The change may be represented as follows:

$$\underset{\begin{bmatrix}\text{copper}\\ \text{oxygen}\end{bmatrix}}{\text{copper oxide}} + \text{hydrogen} \longrightarrow \underset{\begin{bmatrix}\text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{water}} + \text{copper}$$

The water formed collects in the cold portions of the tube *C* near its end. In this experiment the copper oxide is said to undergo *reduction*. Reduction may therefore be defined as the process of withdrawing oxygen from a compound. As we shall see, the term *reduction* is also used with a somewhat different meaning.

Relation of reduction to oxidation. At the same time that the copper oxide is reduced, it is clear that the hydrogen is oxidized, for it combines with the oxygen given up by the copper oxide. The two processes are therefore very closely related, and it usually happens that when one substance is oxidized, some other substance is reduced. The one which gives up its oxygen is called an *oxidizing agent*, while the other, which unites with the oxygen of the oxidizing agent, is called a *reducing agent.*

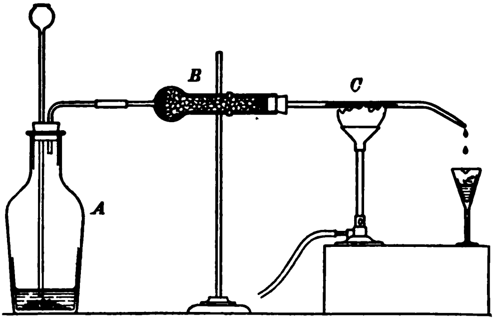


FIG. 19. Reduction of copper oxide by hydrogen

Uses of hydrogen. Hydrogen is sometimes used as a material for the inflation of balloons, but usually the much cheaper coal gas is substituted for it, and even hot air is used when the duration of ascension is very short. It has been used in the oxyhydrogen blowpipe as a source of light and heat. Where the electric current is available, however, the blowpipe has been displaced almost entirely by the electric light and electric furnace, which are more economical and more powerful sources of light and heat. Its greatest commercial use is in the conversion of liquid oils into solid edible fats, as explained later (p. 239).

The oxyhydrogen blowpipe. This is a form of apparatus used for burning hydrogen in pure oxygen. It consists of a small tube placed within a larger one, as shown in Fig. 20. The hydrogen is first passed through the outer tube and ignited at the open end of the tube *A*. The oxygen is then conducted through the inner tube and mixes with the hydrogen at the end of the tube. The intensity of the heat may be shown by bringing into the flame pieces of metal such as iron wire or zinc. These burn with great brilliancy. Even platinum, having a melting point of 1755°, may be melted by the heat of the flame. While the oxyhydrogen flame is intensely hot, it is almost nonluminous. If it is directed against some infusible substance like ordinary lime, the heat is so intense that the lime becomes incandescent and glows with a brilliant light. This is sometimes used as a source of light under the name *limelight*.

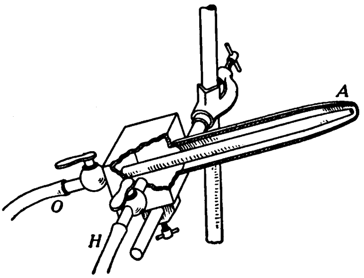


Fig. 20. The oxyhydrogen blowpipe

EXERCISES

1. In Fig. 17 why is it necessary to dry the hydrogen by means of the calcium chloride in the tube *B*?

2. From Fig. 17 suggest a way for determining experimentally the quantity of water formed in the reaction.

3. In Fig. 18 will the flame remain at the mouth of the tube?

4. How many grams of hydrogen can be made from 100 g. of hydrogen sulfate (p. 27)? *Ans.* 2.05 g.

5. How many grams of hydrogen can be made from 100 g. of water? *Ans.* 11.18 g.

Topics for Themes

Cavendish (Thorpe, Essays in Historical Chemistry).

Oxyhydrogen blowpipe (see encyclopedia).

CHAPTER V

THE GAS LAWS; STANDARD CONDITIONS

Introduction. It will be remembered that in discussing the properties of oxygen and hydrogen the weight of a liter of each gas was given. A moment's reflection will make it clear that these weights must refer to some set of arbitrary conditions, for it is a familiar fact that the volume of a given quantity of a gas varies both with changes in pressure and with changes in temperature.

FIG. 21. Robert Boyle (1626–1691)

One of the most accurate of the early chemists

Variation of volume with pressure: law of Boyle. That the volume occupied by a given weight of a gas can be altered by changing the pressure is familiar to everyone who has pumped air into a bicycle or automobile tire. As early as 1660 Robert Boyle, an Irish investigator (Fig. 21), reached the following conclusion, known as Boyle's law: *If the temperature remains constant, the volume occupied by a given weight of a gas is inversely proportional to the pressure.* Thus, if a given weight of a gas occupies a volume of 1000 cc. when subjected to a certain pressure, it will occupy a volume of 500 cc. if the pressure is doubled, or of 2000 cc. if the pressure is diminished to one half. This means that for a given weight of a gas the product of the pressure into the volume will remain constant, no matter how either one may be altered. Designating the pressure and volume under one set of conditions by P and V, and under a different set by P_1 and V_1, Boyle's law may be stated thus:

$$PV = P_1V_1$$

CENTIGRADE AND ABSOLUTE SCALES

Tin	melts
231.9° C.	504.9° A.
Water	boils
100° C.	373° A.
Phosphorus	melts
44° C.	317° A.
Water	freezes
0° C.	273° A.
Mercury	freezes
− 38.7° C.	234.3° A.
Chlorine	freezes
− 101.5° C.	171.5° A.
Oxygen	boils
− 182.9° C.	90.1° A.
Absolute	zero
− 273° C.	0° A.

FIG. 22. Comparison of temperatures on the centigrade and absolute scales

Variation of volume with temperature. If the pressure is held constant, all gases expand when the temperature is raised and contract when it is lowered, and it is a remarkable fact that the volumes of all gases change to the same extent for a given variation in the temperature. Let us suppose that the volume of a gas has been measured at zero on the centigrade scale. Experiment has shown that a rise of one degree causes an expansion of $\frac{1}{273}$ of this volume; a rise of five degrees, an expansion of $\frac{5}{273}$. If we take 273 cc. of this gas at zero, the volume at 1° above will be 274 cc.; at 1° below it will be 272 cc.; and at 5° below it will be 268 cc. At the same rate of contraction the volume will be 1 cc. at − 272°, and at − 273° it will be zero. Of course this cannot really happen, and experiment shows that before this temperature is reached, all gases have changed into liquids or solids. Helium, the most difficult gas to liquefy, passes into a liquid at – 268.7°.

The absolute scale of temperature. If we were to construct a thermometer having divisions of the same size as those on the centigrade scale, but with the zero point at – 273° on the latter scale, then the point at which water freezes (0° centigrade) would be 273°. At 272° on this scale the 273 cc. of gas mentioned in the last paragraph would measure 272 cc.; at 271° it would measure 271 cc.; at 1°, 1 cc. On such a scale the volume of a gas would be proportional to the temperature at every point. This scale is known as the *scale of absolute temperature*, the point – 273° centigrade being the *absolute-zero point*. Evidently the absolute temperature may be obtained by adding 273° to the centigrade reading. Fig. 22 gives a comparison of the centigrade and absolute scales at a number of temperatures.

FIG. 23. Joseph Louis Gay-Lussac (1778–1850)

A distinguished French chemist

The law of Gay-Lussac (or of Charles). A general statement can now be made in regard to the effect of temperature on the volume of a gas: *If the pressure remains constant, the volumes occupied by a given weight of a gas at different temperatures are proportional to the absolute temperatures.*

If V and V_1 are the volumes at the temperatures T and T_1, then $V : V_1 :: T : T_1$,

or
$$V = \frac{V_1 T}{T_1}$$

The above generalization is called the law of Gay-Lussac (Fig. 23) or of Charles, since it was formulated independently by these two Frenchmen in 1801.

Standard conditions. It is now easy to choose conditions which can be regarded as standard for the measurement of gases, and these will be taken for granted unless a special statement to the contrary is made.

As a *standard temperature* the temperature of melting ice is chosen, which is 0° centigrade or 273° absolute.

As a *standard pressure* the average pressure exerted by the atmosphere at sea level has been selected. This is equal to 1033 g. per square centimeter. As a rule, however, the pressure of the atmosphere is expressed by stating the height of a column of mercury which the pressure of the atmosphere will sustain; and, expressed in this way, the standard pressure is equal to that exerted by a column of mercury 760 mm. in height.

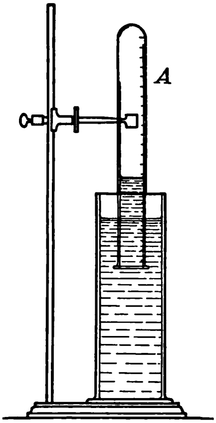


FIG. 24. Measuring a gas collected over water

Aqueous tension. As a rule, gases are measured in the laboratory by collecting them over water in a graduated tube, as represented in Fig. 24. Before the reading is taken, the tube A is first raised or lowered until the level of the water is the same within and without the tube; the inclosed gas is then under atmospheric pressure. But to some extent water has evaporated into the tube, and a part of the volume inclosed *is due to water vapor* and not to the gas. If the water vapor could be removed, the gas would occupy a smaller volume. If we could find out how much pressure the water vapor exerts upon the surface of the water within the tube and subtract this from the atmospheric pressure, we should have the pressure which the gas itself exerts at the volume which it occupies. The pressure due to the water vapor is called the *aqueous tension* or the *vapor pressure.* It increases steadily as the temperature rises, and the table in the Appendix gives its value over the range of temperatures most required.

Kinetic molecular theory. It is a surprising fact that all gases should exert a considerable pressure when confined in a closed vessel, and that the volume of all gases should be equally affected by changes in pressure and temperature. These facts have led to the view that all gases are made up of minute particles, called *molecules*, which are in very rapid motion. Their momentum, as they strike the walls of the confining vessel, occasions the pressure which the gas exerts. This conception is called the *kinetic molecular theory.*

Examples of calculation. A few typical examples of the application of the gas laws to actual calculations will make their meaning clear. (It will be understood that temperatures are always given on the centigrade scale unless otherwise specified.)

1. A gas measured under a pressure of 720 mm. had a volume of 620 cc. What volume will this gas occupy under standard pressure, 760 mm., the temperature remaining constant?

According to Boyle's law, $PV = P_1V_1$. Substituting the values given in the problem, we have $760\ V = 720 \times 620$; or $V = 587.4$ cc.

2. The volume of a gas measured at a temperature of 90° is 930 cc. What will be its volume at 0°, the pressure remaining constant?

According to the law of Gay-Lussac, $V : V_1 :: T : T_1$, in which T and T_1 refer to the absolute scale. Changing the centigrade temperatures, given in the problem, to absolute temperatures by adding 273, and substituting in the formula, we have

$$V : 930 :: 273^\circ : 363^\circ; \text{ or } V = 699.1 \text{ cc.}$$

3. A gas measured 300 cc. under a pressure of 740 mm. and a temperature of 25° (or 298° absolute scale). What will its volume be under standard conditions (0° and 760 mm. pressure)?

First find the change in volume due to change in pressure:

$$300 \times 740 = 760 \times V; \text{ or } V = 292 \text{ cc.}$$

Next make the correction for temperature:

$$292 : V :: 298 : 273; \text{ or } V = 264.5 \text{ cc.}$$

This gives the volume under standard conditions.

When the gas volumes are measured over water, the value of the aqueous tension (see Appendix) must be subtracted from the barometric pressure. For example, suppose that, in problem 3 above, the gas had a volume of 300 cc. when measured over water (Fig. 24); the pressure would not then be 740 mm. but 740 less 23.69, which is the value for the aqueous tension at 25°. The real pressure, therefore, is $740 - 23.69$, or 716.31 mm. The problem is then solved just as above, except that the value 716.31 is substituted for the value 740.

Practical suggestions. In solving such problems the student should notice that an increase of pressure diminishes the volume, as does also a decrease in temperature. After solving a problem, he should compare his results with the original values and see if they are reasonable. It will be of assistance to remember that if the conditions under which a gas is measured are actual laboratory conditions (pressure from 740 to 760 mm. and temperature from 15° to 25°), the gas will contract at standard conditions to from about 7 to 12 per cent.

EXERCISES

1. Give two illustrations of Boyle's law from everyday experience.

2. Why is the bottom of a balloon left open and not tightly closed?

3. How does the air brake on a railway car work?

4. How do you change readings on the Fahrenheit scale into centigrade readings?

5. On warm, humid days an automobile engine will not work as smoothly (without adjustment) as on cold, dry ones. Why is this?

6. Why does a balloon tend to fall toward evening and rise at midday?

7. A gas under standard pressure measured 780 cc. Temperature remaining constant, what will be the pressure when the volume measures 360 cc.? *Ans.* 1646.6 mm.

8. A gas at 0° measured 560 cc. Under the same pressure what will be its volume at 100°? *Ans.* 765.1 cc.

9. Under standard conditions a gas measured 950 cc. What will be its volume at 740 mm. and 22°? *Ans.* 1054.3 cc.

10. A gas standing over water at 20° with the barometer reading 755 mm. measured 100 liters. Without change in temperature or barometric pressure, the gas was passed through a drying agent and collected over mercury. What was its volume? *Ans.* 97.68 liters.

11. 100 g. of potassium chlorate and 25 g. of manganese dioxide were heated in the preparation of oxygen. What products were left in the flask, and how much of each was present? *Ans.* 60.8 g. of potassium chloride and 25 g. of manganese dioxide.

TOPICS FOR THEMES

Robert Boyle (Thorpe, Essays in Historical Chemistry).

Gay-Lussac (see encyclopedia).

The different thermometers in common use (see encyclopedia).

CHAPTER VI

COMPOUNDS OF HYDROGEN AND OXYGEN: WATER AND HYDROGEN PEROXIDE

WATER

Historical. Water was regarded as an element until 1781, when Cavendish showed that it is formed by the union of hydrogen and oxygen. Being a believer in the phlogiston theory, however, he failed to interpret his results correctly. A few years later Lavoisier repeated Cavendish's experiments and showed that water must be regarded as a compound of hydrogen and oxygen.

Occurrence of water. Water not only covers about five sevenths of the surface of the earth and is present in the atmosphere in the form of vapor, but it is also a common constituent of the soil, of many rocks, and of almost every form of animal and vegetable organism. Nearly 70 per cent of the human body is water. This is derived not only from the water which we drink but also from the food which we eat, most of which contains a large percentage of water. The table on page 241 shows the percentage of water present in some of the more common foods.

Composition of natural waters. Water as it occurs in nature always contains more or less matter derived from the rocks and soils with which it comes in contact. When such water is evaporated, this matter is left behind in solid form. Even rain water, which is the purest natural water, contains dust particles and gases dissolved from the atmosphere. The foreign matter in natural waters is of two kinds, namely, *mineral* and *organic.*

1. ***Mineral matter.*** The mineral substances ordinarily present in fresh waters are common salt and compounds of calcium, magnesium, and iron. Water containing any considerable amounts of mineral matter does not form a lather with soap, and is termed *hard water.* Water containing little or no mineral matter, such as rain water, is termed *soft water.* One liter of an average river water contains about 9.175 g. of mineral matter. The waters of the ocean contain about 40 g. of mineral matter to the liter, more than three fourths of which is common salt.

2. ***Organic matter.*** The organic matter present in water consists of products derived from animal and vegetable life. Such matter is absorbed from the soil or introduced from sewage. Associated with such matter and feeding upon it are certain living microörganisms.

Effect of the foreign matter in water upon health. As a rule, any sickness resulting from drinking impure waters is due to the presence of living microörganisms. Many of these are without injurious effect upon the human system, but some are the direct cause of disease. Thus, a transmissible disease such as typhoid fever is due to a certain kind of organism which, through food or drink, is introduced into the system. *It is easily possible for these organisms to find their way, through sewage, from persons afflicted with the disease into wells or any poorly protected water supply, and it is chiefly in this way that typhoid fever is spread.*

Purification of water. Three general methods are used for the purification of water, namely, *distillation, boiling,* and *filtration.*

1. ***Distillation.*** The most effective way of purifying ordinary water is by the process of distillation. This consists

in boiling the water and condensing the resulting steam. In the laboratory the process is usually conducted as follows:

Ordinary water is poured into the flask *A* (Fig. 25) and boiled. The steam is conducted through the condenser *B*, commonly known as a Liebig condenser, which consists essentially of a narrow glass tube sealed within a larger one, the space between the two being filled with cold water, which enters at *C* and escapes at *D*. In this way the inner tube is kept cool and the steam in passing through it is condensed. The water formed by the condensation of the steam collects in the receiver *E* and is known as *distilled water*. The impurities are not changed into vapor but remain in the flask *A*.

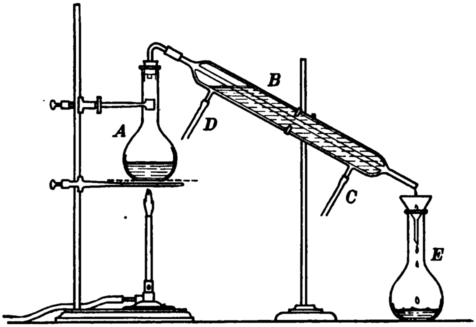


FIG. 25. The distillation of water in the laboratory

Distilled water is pure water. It is used by the chemist in almost all of his work. Large quantities are also used in the manufacture of ice, as well as for drinking.

Commercial distillation. In preparing distilled water on a large scale the steam is generated in a metal boiler *A* (Fig. 26) and is conducted through the pipe *B* to the condensing coil *C*, made of tin. This pipe is wound into a spiral and is surrounded by cold water, which enters at *D* and flows out at *E*. The distilled water is collected in a suitable container *F*.

2. ***Boiling.*** In purifying water for drinking purposes it is only necessary to remove or destroy the microörganisms

present. When the amount of water to be purified is small, as is the case with the household supply for drinking, this is most conveniently accomplished by boiling the water for ten or fifteen minutes. While the organisms are destroyed in a short time by moist heat, even severe cold has been found to have comparatively little effect upon them.

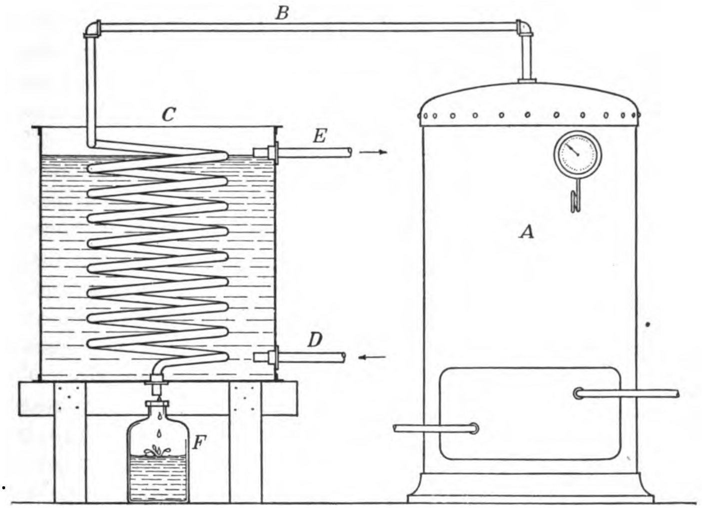


FIG. 26. The commercial distillation of water

3. ***Filtration.*** On a small scale, water is filtered in two ways: (1) by passing it through some porous material, such as charcoal, or (2) by forcing it through porous clay ware, as is done in the Chamberlain-Pasteur filter. While such filters, if kept clean and in good condition, remove most of the organic matter, they do not remove mineral matter except such as is held in suspension. These household filters are not easily kept in order and soon become ineffective. They are no longer used to any great extent.

City filtration. Many cities find it necessary to take their water supply from rivers. The rivers, especially in thickly populated districts, are almost certain to be contaminated with organic matter, suggesting the possible presence of disease germs. Such water is a constant menace to the health of the city, so that it is of the greatest importance to find some way of purifying it effectively on a large scale. This is done by filtration. Two general kinds of filters are in use:

1. ***Slow sand filters*** (Fig. 27). These consist of large beds of sand and gravel, through which the water passes slowly. Some of the impurities are strained out, while others are decomposed by the action of certain kinds of microörganisms which collect in a jellylike layer on the surface of the filter. The purified water passes into the porous pipe *A*, from which it is pumped into the city mains. The filters are covered to protect the water and prevent it from freezing.

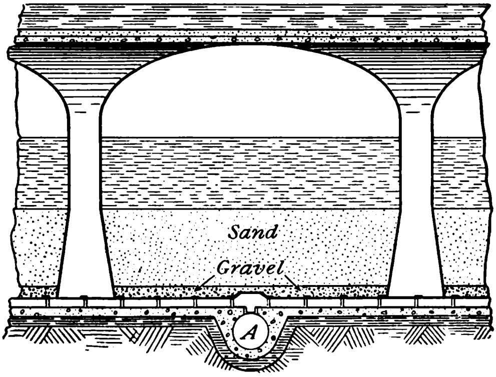


FIG. 27. A covered sand-filter bed

2. ***Mechanical filters.*** In these the water, before filtration, is run into large tanks and treated with certain compounds, such as aluminium sulfate or iron sulfate, which form in the water a small amount of gelatinous solid. This slowly settles to the bottom (p. 328), carrying with it much of the organic matter present. The partially clarified water is then filtered through sand and gravel. In the United States about 400 cities and towns are filtering their water supply, 350 of which are using the mechanical filters.

The effect of the filtration of the water supply upon the health of a city is shown by the fact that in general the number of cases of typhoid fever in cities which have introduced an effective water-purification system has been decreased by about 75 per cent. The number of cases of many other diseases has been likewise diminished.

Self-purification of water. It has long been known that water contaminated with organic matter tends to purify itself when exposed to the air (p. 22). This is due to the fact that air is somewhat soluble in water and that the dissolved oxygen, in the presence of certain microörganisms, gradually oxidizes the organic matter present in the water; when this is destroyed, the organisms present die for lack of food. While water is undoubtedly purified in this way, the process cannot be relied upon to purify a contaminated water so as to render it safe for drinking purposes.

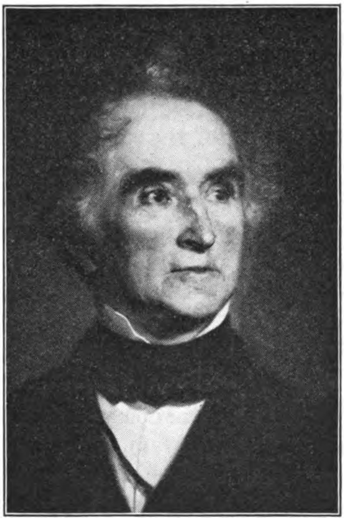


FIG. 28. Justus Liebig (1803-1873)

A great German chemist and teacher. A pioneer, especially in agricultural chemistry

Properties of water. Pure water is an odorless and tasteless liquid, colorless in thin layers but having a bluish tinge when observed through a considerable thickness. It solidifies at 0° and boils at 100° under the normal pressure of 1 atmosphere. When water is cooled, it steadily contracts until the temperature of 4° is reached; at lower temperatures it expands. Water is remarkable for its ability to dissolve other substances, and is the most general *solvent* known. Chemists usually employ aqueous solutions of substances rather than the substances themselves, since as a rule chemical action takes place more readily in solution.

Chemical conduct. Water is a very stable substance; in other words, it does not undergo decomposition readily. To decompose it into its elements by heat alone requires a very high temperature. Even at 2500° only about 10 per cent of the water heated is decomposed. Though very stable toward heat, water can be decomposed in other ways, as by the action of the electric current or by certain metals.

Though containing 88.81 per cent of oxygen, water is not a good oxidizing agent, because of its great stability. However, certain metals, as well as carbon, can be oxidized by very hot steam, the hydrogen being set free. Water combines directly with many compounds, forming substances called *hydrates*. Blue vitriol and alum are good examples of such hydrates.

Heat of formation and heat of decomposition are equal. The fact that a very high temperature is necessary to decompose water into hydrogen and oxygen is in accord with the fact that a great deal of heat is evolved by the union of hydrogen and oxygen (p. 32), for it has been proved that the heat necessary to decompose a compound into its elements (heat of decomposition) is equal to the heat evolved in the formation of the same compound from its elements (heat of formation).

The determination of the exact composition of water. To determine the quantitative composition of a compound, such as water, we must first ascertain what particular elements are present in it and then the proportion in which these elements are united. We have already shown that water is composed of hydrogen and oxygen (Figs. 17 and 19). It remains for us to determine in what ratio these elements are combined in the compound.

The proportion in which hydrogen and oxygen combine to form water. By mixing known volumes of hydrogen and oxygen, causing them to combine, and then ascertaining the volume and identity of the gas remaining, it is possible to determine the exact proportion in which the two gases combine to form water. Such a process is called a *synthesis*, and it may be carried out as follows:

Details of the experiment. The combination of the two gases is brought about in a tube called a *eudiometer*. This is a graduated glass tube about 60 cm. long and 2 cm. wide, closed at one end (Fig. 29). Near the closed end two platinum wires are fused through the glass, the ends of the wires within the tube being separated by a space of 2 or 3 mm. The tube is entirely filled with mercury and inverted in a vessel of the same liquid. Pure hydrogen is passed into the tube until it is about one fourth filled. The tube is then lowered until the mercury stands at the same level inside and outside the tube, and the reading of the volume of the hydrogen is taken. Approximately an equal volume of pure oxygen is then introduced, and the volume is again taken. This gives the total volume of the two gases. From this the volume of the oxygen introduced may be determined by subtracting from it the volume of the hydrogen.

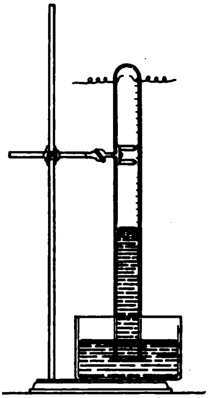


FIG. 29. The eudiometer employed in determining the composition of water

The combination of the two gases is now brought about by connecting the two platinum wires with an induction coil and passing a spark from one wire to the other. Immediately a slight explosion occurs. The mercury in the tube is at first depressed because of the expansion of the gases due to the heat generated, but it at once rebounds, taking the place of the gases which have combined to form water. The volume of the water in the liquid state is so small that it may be disregarded in the calculations.

In order that the temperature of the residual gas and the mercury may become uniform, the apparatus is allowed to stand for a few minutes, and the volume of the gas is taken. The residual gas is then tested in order to ascertain whether it is hydrogen or oxygen, since experiments have proved that it is never a mixture of the two. From the information thus obtained the composition of the water may be calculated.

Calculation of composition. Thus, suppose the readings were as follows:

Volume of hydrogen	20.3 cc.
Volume of hydrogen and oxygen	38.7 cc.
Volume of oxygen	18.4 cc.
Volume of gas left after combination has taken place (found to be oxygen)	8.3 cc.

We have thus found that 20.3 cc. of hydrogen have combined with 18.4 cc. minus 8.3 cc. (or 10.1 cc.) of oxygen; or approximately 2 volumes of hydrogen have combined with 1 volume of oxygen. Since oxygen is 15.9 times as heavy as hydrogen, the proportion by weight in which the two gases combine is 1 part of hydrogen to 7.94 parts of oxygen.

Method used by Berzelius and Dumas. The method used by these investigators enables us to determine directly the proportion by weight in which the hydrogen and oxygen combine.

Details of the experiment. Fig. 30 illustrates the essential parts of the apparatus used in making the determination. The glass tube *B* contains copper oxide, while the tubes *C* and *D* are filled with calcium chloride, a substance which has great affinity for water. The tubes *B* and *C*, including their contents, are carefully weighed, and the apparatus is connected as shown in the figure. A slow current of pure hydrogen is then passed through *A*, and that part of the tube *B* which contains copper oxide is carefully heated. The hydrogen combines with the oxygen of the copper oxide to form water, which is absorbed by the calcium chloride in tube *C*. The calcium chloride in tube *D* prevents any moisture entering tube *C* from the air. The operation is continued until an appreciable amount of water has been formed. The tubes *B* and *C* are then weighed once more. The loss of weight in the tube *B* will exactly equal the weight of oxygen taken up from the copper oxide in the formation of the water. The gain in weight in the tube *C* will exactly equal the weight of the water formed. The difference in these weights will of course equal the weight of the hydrogen present in the water formed during the experiment.

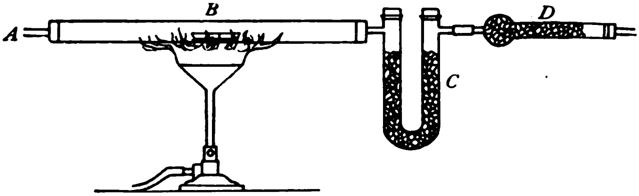


FIG. 30. Apparatus employed in determining the ratio by weight in which oxygen and hydrogen combine

Dumas's results. The above method for the determination of the composition of water was first used by Berzelius in 1820. The work was repeated in 1843 by Dumas, who obtained the following results:

Weight of water formed	945.439 g.
Oxygen given up by the copper oxide . . .	840.161 g.
Weight of hydrogen present in water . . .	105.278 g.

According to this experiment the ratio of hydrogen to oxygen in water is 105.278 : 840.161, or 1 : 7.98.

Morley's results. In recent years the American chemist Morley has determined the composition of water with great care. Extreme precautions were taken to use pure materials and to eliminate all sources of error. The hydrogen and oxygen which combined, as well as the water formed, were all accurately weighed. According to Morley's results, 1 part by weight of hydrogen combines with 7.94 parts by weight of oxygen to form water.

Comparison of results obtained. From the above discussion it is easy to see that it is by experiment alone that the composition of a compound can be determined. Different methods may lead to slightly different results. The more accurate the method chosen, and the greater the skill with which the experiment is carried out, the more accurate will be the results. It is generally conceded by chemists that the results obtained by Morley in reference to the composition of water are the most accurate ones. In accordance with these results, then, water must be regarded as a compound containing hydrogen and oxygen in the ratio of 1 part by weight of hydrogen to 7.94 parts by weight of oxygen.

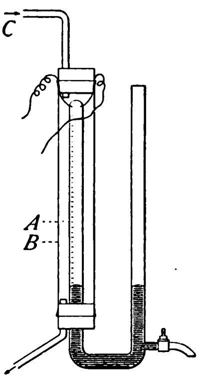


Fig. 31. Eudiometer for measuring the volume of steam formed by the union of oxygen and hydrogen

Relation between the volume of aqueous vapor and the volumes of the hydrogen and oxygen which combine to form it. If the quantitative synthesis of water as described above (Fig. 29) is carried out at a temperature above 100°, the water vapor formed is not condensed, and it thus becomes possible to compare the volume of the water vapor with the volumes of hydrogen and oxygen which combined to form it. This can be accomplished by surrounding the upper part of the eudiometer *A* (Fig. 31) with a glass tube *B*, through which is passed at *C* the vapor obtained by boiling some liquid which has a boiling point above 100°. This vapor keeps the tube *A* heated above the boiling point of water. In this way it has been proved that 2 volumes of hydrogen and 1 volume of oxygen combine to form exactly 2 volumes of water vapor. *It will be noted that the relation between these volumes may be expressed by whole numbers.* The significance of this very important fact will be discussed in a subsequent chapter.

Law of definite composition. We have just seen that water contains hydrogen and oxygen combined in a perfectly definite ratio. In the earlier days of chemistry there was much discussion as to whether the composition of a given compound is always precisely the same or whether it is subject to some variation. Experiments have shown, however, that the composition of a pure chemical compound is always exactly the same. Thus, pure water obtained from any source whatever, such as melting pure ice, condensing steam, or burning hydrogen in oxygen, always contains 1 part by weight of hydrogen to 7.94 parts of oxygen. This truth is known as the *law of definite composition* and may be stated thus: *The composition of a chemical compound never varies.*

HYDROGEN PEROXIDE

Composition. As has been shown, 1 part by weight of hydrogen combines with 7.94 parts by weight of oxygen to form water. It is possible, however, to obtain a second compound of hydrogen and oxygen differing from water in composition in that 1 part by weight of hydrogen is combined with 2 × 7.94, or 15.88, parts of oxygen. This compound is called *hydrogen peroxide*, the prefix *per-* signifying that it contains more oxygen than hydrogen oxide, which is the chemical name for water.

Preparation. Hydrogen peroxide is prepared by the action of acids upon barium peroxide. When sulfuric acid is used, the change which takes place may be indicated as follows:

$$\begin{array}{ccccccc} \left.\begin{array}{l}\text{barium}\\ \text{peroxide}\end{array}\right\} & + & \left\{\begin{array}{l}\text{sulfuric}\\ \text{acid}\end{array}\right\} & \longrightarrow & \left\{\begin{array}{l}\text{barium}\\ \text{sulfate}\end{array}\right\} & + & \left\{\begin{array}{l}\text{hydrogen}\\ \text{peroxide}\end{array}\right. \\ \begin{bmatrix}\text{barium}\\ \text{oxygen}\end{bmatrix} & & \begin{bmatrix}\text{hydrogen}\\ \text{sulfur}\\ \text{oxygen}\end{bmatrix} & & \begin{bmatrix}\text{barium}\\ \text{sulfur}\\ \text{oxygen}\end{bmatrix} & & \begin{bmatrix}\text{hydrogen}\\ \text{oxygen}\end{bmatrix} \end{array}$$

Properties and chemical conduct. Hydrogen peroxide is a clear, sirupy liquid having a density of 1.458. It is difficult to prepare in a pure state, since it is very unstable, decomposing into water and oxygen with explosive violence:

$$\text{hydrogen peroxide} \longrightarrow \text{water} + \text{oxygen}$$

In dilute solution it is fairly stable, although it should be kept in a dark, cool place; otherwise the solution loses its strength, the hydrogen peroxide present gradually decomposing into water and oxygen. The presence of a small percentage of certain substances, such as a trace of acid, preserves the strength by retarding decomposition.

Uses. Solutions of hydrogen peroxide are used largely as oxidizing agents. The solution sold by druggists contains 97 per cent water and 3 per cent of the peroxide, and is used in medicine as an antiseptic. Its use as an antiseptic depends upon its oxidizing properties. It acts upon certain dyes and natural colors, such as that of the hair, oxidizing them to colorless compounds; hence it is sometimes used as a bleaching agent. A stronger solution (30 per cent) is used as an oxidizing agent in certain chemical operations.

The law of multiple proportion. It has been shown that both water and hydrogen peroxide are compounds of hydrogen and oxygen, and that the ratio by weight in which these two elements are present in each of these compounds is as follows:

Water	hydrogen : oxygen : : 1 : 7.94
Hydrogen peroxide . . .	hydrogen : oxygen : : 1 : 15.88

It will be seen that the ratio between the weights of oxygen combined with a fixed weight of hydrogen (say 1 g.) in these two compounds is 7.94 : 15.88, or 1 : 2.

Similarly, many elements other than oxygen and hydrogen unite to form a number of distinct compounds, each with its own precise composition. In all such compounds the same statement holds as in the case of water and hydrogen peroxide — the weights of the one element which are combined with a fixed weight of the other always bear a simple ratio to each other, such as 1 : 2 or 2 : 3. This truth is known as the *law of multiple proportion.* It was formulated by John Dalton (p. 67) in 1808, and may be stated thus: *When any two elements, A and B, combine to form more than one compound, the weights of A which unite with any fixed weight of B bear the ratio of small whole numbers to each other.*

EXERCISES

1. In making solutions why does the chemist use distilled water rather than filtered water?

2. How could you determine the total amount of solid matter dissolved in a sample of water?

3. How could you determine whether a given sample of water is distilled water?

4. How could the presence of air dissolved in water be detected?

5. How could the amount of water in a food such as bread or potato be determined?

6. Would ice frozen from impure water necessarily be free from disease germs?

7. Suppose that the maximum density of water were at 0° instead of at 4°. What effect would this have on the formation of ice on bodies of water?

8. Why is it that merely heating water to the boiling point is not sufficient to render it safe for sanitary purposes?

9. If steam is heated to 2000° and again cooled, has any chemical action taken place?

10. Why is cold water passed into *C* instead of *D* (Fig. 25)?

11. Mention at least two advantages that a metal condenser has over a glass condenser.

12. Draw a diagram of the apparatus used in your laboratory for supplying distilled water.

13. 20 cc. of hydrogen and 7 cc. of oxygen are placed in a eudiometer and the mixture exploded. How many cubic centimeters of aqueous vapor are formed? *Ans.* 14 cc. What gas and how much of it remains in excess? *Ans.* 6 cc. hydrogen.

14. What weight of oxygen is contained in 100 g. of water? *Ans.* 88.81 g. In 100 g. of pure hydrogen peroxide? *Ans.* 94.07 g.

TOPICS FOR THEMES

Methods used in your city for obtaining pure water.

Comparison of the properties of water with those of the gases from which it is formed.

CHAPTER VII

MATTER AND ENERGY

Definition of matter. The term *matter* includes everything that occupies space and possesses weight or mass. The word therefore applies equally to the gases of the atmosphere, the water of the ocean, and all the solid objects which make up the world.

Conservation of matter. The facts we have learned about burning, and the experiments we have made with oxygen and hydrogen, have taught us that matter may undergo many transformations as a result of chemical action, and that many of its properties change as a result of such action. One property alone never changes, and that is the *mass.* This very important fact was first clearly recognized by Lavoisier, and a general statement of it is known as the law of conservation of matter. The law may be stated thus: *During all the changes through which a given quantity of matter may pass, its mass remains constant.*

States of matter. We have found that water may appear in three very different conditions, depending upon the temperature, namely, solid, liquid, and gaseous. These are called the three *states* of matter. This is not a peculiarity of water, for all substances exist in all three states, save only when the temperature required for the melting of the solid or the vaporization of the liquid is so high that decomposition takes place before the change is effected. Thus, we have seen that mercuric oxide decomposes before it melts. Potassium chlorate can be melted without difficulty, but it decomposes before it boils.

The freezing and melting points. A solid normally passes into a liquid at a perfectly definite temperature, called its *melting point.* A given weight of any solid, in melting, absorbs a definite quantity of heat, the exact amount absorbed depending upon the solid. This is known as the *heat of fusion.* On the other hand, the liquid formed tends to pass back into the solid state at this same temperature, called the *freezing point,* and in so doing the heat of fusion is given out again. In this case it is called the *heat of solidification.* For example, water freezes and ice melts at the same temperature, namely, 0°. Moreover, 1 g. of ice at 0°, in melting, absorbs a quantity of heat that would raise the temperature of 1 g. of water from 0° to 79°, while 1 g. of water at 0°, in freezing, gives out this same quantity of heat.

Sometimes it is possible to cool the liquid below the freezing point, and it is then said to be *undercooled.* If a fragment of the solid is placed in the undercooled liquid, solidification will at once begin, and the temperature will rise to the true freezing point and remain there as solidification continues. The freezing point is therefore best defined as the temperature at which the liquid and the solid can be mixed without change in temperature.

Vaporization. There is no definite temperature at which a liquid passes into a vapor, or gas. Water exposed to the air vaporizes at all temperatures, and even ice and snow evaporate during weather in which no melting occurs. The higher the temperature the more rapid the evaporation.

Boiling point. The escape of vapor from an open vessel containing a liquid is hindered by the air which presses upon the surface of the liquid. The vapor escapes by making its way slowly through the air, but when the vapor pressure just exceeds the pressure exerted by the air, there is nothing to prevent the vapor from making its escape as fast as it forms, pushing the air before it. When this is the case, any additional heat applied to the liquid will not raise its temperature, but will merely increase its rate of evaporation.

This temperature is called the *boiling point* of the liquid, and *the boiling point may be defined as the temperature at which the vapor pressure of the liquid just exceeds the pressure of the atmosphere.* It will be noticed that the boiling point of a liquid is not fixed, but depends upon the atmospheric pressure.

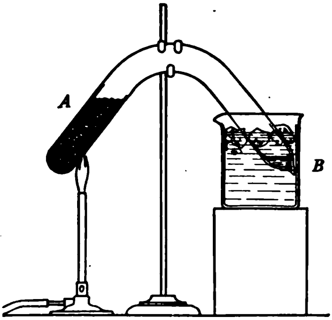


FIG. 32. Faraday's method of liquefying gases

Liquefaction of gases. Since increase of pressure tends to raise the boiling point of a liquid, it is clear that pressure applied to a gas will tend to condense it into a liquid. Faraday (Fig. 33), beginning about 1832, was the first to apply this principle in an attempt to liquefy gases, and he succeeded in liquefying many gaseous substances which up to that time had never been prepared in the liquid state.

Method of Faraday. Faraday's method was to select some solid which, on being heated, gives off a gas. Some of the solid was placed in one limb, *A*, of a bent tube (Fig. 32), the tube was then sealed, and the other limb, *B*, was placed in ice water. When the solid was heated, the gas was given off in a closed space, and the pressure which it exerted liquefied a portion of the gas in the cold part of the tube.

Liquid-air machines. Later it was found that to liquefy any given gas it must be cooled below a certain temperature, which varies from gas to gas and which is known as the *critical temperature* of the gas. Machines are now made which simultaneously compress the gas and cool it, and all gases, even air and hydrogen, have now been liquefied.

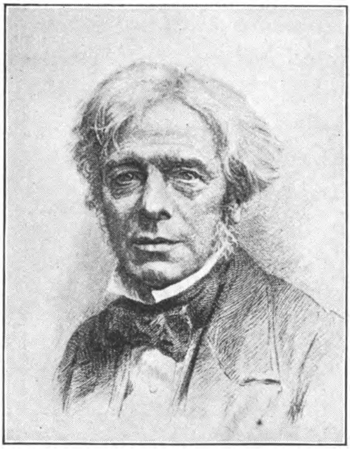


FIG. 33. Faraday (1794–1867)

An English scientist, who devised methods for liquefying gases

Amorphous and crystalline matter. Sometimes the particles of which a piece of solid matter is composed have no definite form and, even under the microscope, have no sharp edges or flat surfaces. Such solids are said to be *amorphous.*

More often a careful examination of a solid will show that it is made up of a great many particles, each of which has sharp edges and flat surfaces. Such solids are said to be *crystalline*, and each individual piece is called a *crystal.* While crystals have a great variety of forms, yet for any given substance the crystalline form is perfectly definite. Crystals range in size from microscopic to very large, a single quartz crystal found in California weighing over a ton.

Although there are a great many forms of crystals, they can all be considered as varieties of only a few fundamental ones, and a study of the relations of all these forms to the fundamental ones constitutes the science of *crystallography.* In describing crystals we shall not attempt to employ the terms of crystallography, but shall use such terms as *needle-shaped*, *flat plates*, *cubes*, and *octahedra*. A few well-formed crystals are shown in Fig. 34.

Heat. Now that we have considered two elements, oxygen and hydrogen, and the compounds which they form with each other, the question naturally arises, What is the source of the heat which is given off when these elements combine, what is its nature, and how can it be measured? Two facts which have been demonstrated by experiment are of great importance in answering these questions.

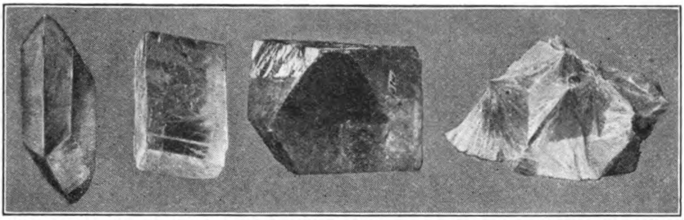


FIG. 34. Some examples of well-formed crystals

Heat has no weight. One of the most striking characteristics of heat is that it has no weight, in which respect it differs from matter of any kind. After a chemical action in which a great deal of heat is set free, the products weigh just the same as the original materials. This can be shown by causing the reaction to take place in a sealed vessel and weighing it before and after the action.

Transformations of heat. A second remarkable fact about heat is that it can be changed into other things, such as the motion of bodies and the electric current, and that these in turn may be changed again into heat. Thus, the heat of the flame *A* (Fig. 35) may be transformed into motion by the engine *B*. The motion of the engine may be used to generate an electric current in the dynamo *C*, and this current may produce light and heat in the lamp *D* and also bring about chemical decomposition of water into oxygen and hydrogen in the cell *E*.

Heat a form of energy. All of these things — heat, mechanical motion, electric current, and light — are called *energy*. The mechanical energy of moving bodies is constantly employed in doing work, and anything that can do work is said to possess energy. Since all other forms of energy can be transformed into mechanical energy, we may say that *energy is the capacity for doing work. Heat is therefore one of the forms of energy.*

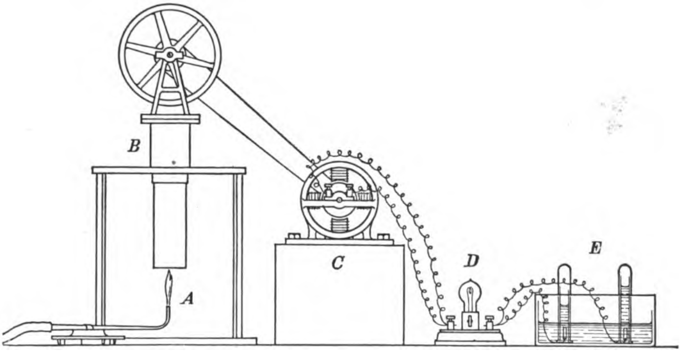


FIG. 35. Diagram illustrating the transformations of heat

Conservation of energy. Most careful experiment has shown that *while energy can be changed from one form into another, or transferred from one body to another, the total quantity remains the same.* This statement is known as the law of conservation of energy. For example, a definite quantity of electrical energy will give a definite quantity of heat or power, otherwise we could not agree upon a price to pay for it. Conversely, when we find heat appearing under any circumstances, we may be quite sure that energy in some other form has been used up. Thus, a hot box on a car is at the expense of work done by the engine.

Chemical energy. When oxygen and hydrogen combine, a great deal of heat is given off, yet there is no very evident form of energy which is used up. Likewise, when the electric current decomposes water into oxygen and hydrogen, electrical energy is used up, and our experience tells us that it must be converted into some other form of energy. We assume that oxygen and hydrogen possess some kind of energy which is changed into heat when they unite. When they are parted again, this energy is restored at the expense of electrical energy or heat. This form of energy is called *chemical energy.* It is this form of energy which all fuels possess and for which we pay when we purchase coal or wood or gas.

Chemical action. When the chemical energy of a substance is changed, we say that *chemical action* has taken place. It is not always easy to be sure that this has occurred, for the change in temperature which we observe may be due to the conversion of some other kind of energy into heat. If, however, a new substance is formed, we may be sure that chemical action has taken place in its formation. (Review page 9.)

Unit of heat. Before a method for measuring heat can be devised, it is necessary to fix upon a unit by which it can be measured. The unit of heat is called a *calorie. The calorie is defined as the quantity of heat required to raise the temperature of one gram of water through one degree.*

Measurement of heat. Matter in any form can be weighed on a balance, but the measurement of heat is not so simple. It is accomplished by causing the heat to be used up in raising the temperature of a weighed quantity of pure water. The apparatus in which this is done is called a *calorimeter* and is represented in Fig. 36. The reaction takes place in solution in the vessel *A*, and the heat given off is used up in raising the temperature of the water contained in it, the rise being read on the thermometers *D*, *D*. The water in *B* serves to prevent absorption of heat from the air.

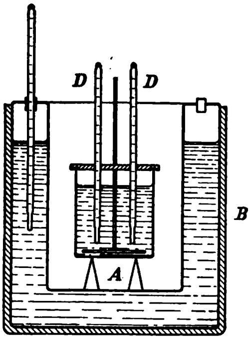


FIG. 36. A calorimeter

Ozone. Sometimes chemical energy may be added to a substance in such a way as to make a great change in its properties and chemical activity while not altering its percentage composition. Thus, if electric sparks are passed through oxygen or air, a small percentage of the oxygen is converted into a substance called *ozone*. The same change can also be brought about by certain chemical processes. For example, if some pieces of phosphorus are placed in a bottle and partially covered with water, the presence of ozone may soon be detected in the air contained in the bottle.

The formation of ozone. The formation of ozone may be shown by partially covering with water a few pieces of stick phosphorus placed in the bottom of a jar (Fig. 37). The slow oxidation of the cold phosphorus is attended by the conversion of some oxygen into ozone. The presence of ozone in the air in the jar is soon indicated by its characteristic odor, as well as by the property it possesses of imparting a blue color to strips of paper, *A*, previously dipped into a solution of potassium iodide and starch.

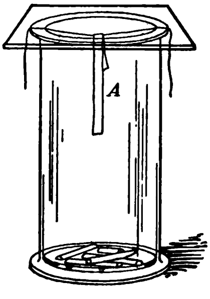


FIG. 37. The formation of ozone by the slow oxidation of phosphorus

The conversion of oxygen into ozone is attended by a change in volume, 3 volumes of oxygen forming 2 volumes of ozone. If the resulting ozone is heated to about 300°, the reverse change takes place, the 2 volumes of ozone being changed into 3 volumes of oxygen. It is possible that traces of ozone exist in the atmosphere, although its presence there has not been definitely proved.

Properties. Ozone is a gas which has the characteristic odor noticed about electrical machines when in operation. When subjected to great pressure and a low temperature the gas condenses to a bluish liquid, boiling at – 119°. Its chemical conduct is similar to that of oxygen except that it is far more active. Air or oxygen containing a small percentage of ozone is now used in place of oxygen in certain manufacturing processes and as a disinfectant. It is also used to some extent in the purification of water, its strong oxidizing properties being sufficient to destroy the microorganisms present.

EXERCISES

1. Name three substances which cannot be melted without decomposition.

2. Name three substances which cannot be boiled without decomposition.

3. When a pond begins to freeze in winter, why does not all the water freeze?

4. Why does a block of ice melt so slowly even in warm air?

5. What becomes of the heat applied to a boiling liquid?

6. Why is it necessary to boil eggs longer on a mountain top than at the seashore in order to cook them?

7. Name three crystalline substances.

8. Give five illustrations of transformation of energy in daily experience.

9. What becomes of the energy of burning coal in a locomotive?

10. Suggest three ways of generating heat. What is the source of energy in each case?

11. Suppose ice and water to be mixed together at 0°. Under what conditions will more water freeze? more ice melt?

12. Suggest a method of raising the boiling point of water above 100°.

13. When water freezes in a bottle, why does it break the bottle?

14. Why is oil used in machinery?

15. How many calories of heat are given off in the freezing of 500 g. of water at 0°? *Ans.* 39,500 cal.

16. In a certain experiment 2250 g. of water at 20° was contained in a calorimeter. After a reaction the temperature was at 24.2°. How much heat was evolved? *Ans.* 9450 cal.

TOPICS FOR THEMES

Michael Faraday (Thorpe, Essays in Historical Chemistry).

Crystals (see encyclopedia).

CHAPTER VIII

COMBINING WEIGHTS; THE ATOMIC THEORY

Introduction. We have already considered three laws which deal with the relations by weight which hold good during chemical action: (1) the law of conservation of matter, (2) the law of definite composition, (3) the law of multiple proportion. To these must now be added a fourth — the law of combining weights.

Combining weights. We have seen that hydrogen and oxygen combine in two perfectly definite ratios by weight, namely, 1 : 7.94 and 1 : 2 × 7.94. In a similar way it is easy to determine the ratios in which elements other than oxygen combine with hydrogen. For example, hydrogen combines with sulfur to form a gas called *hydrogen sulfide*, and with the metal calcium to form a solid called *calcium hydride*. In these compounds the ratios by weight are

Hydrogen sulfide	hydrogen 1, sulfur 16
Calcium hydride	hydrogen 1, calcium 19.88

It is therefore possible to assign to each element combining with hydrogen a number which expresses the weight in grams of the element which combines with 1 g. of hydrogen.

Now experiment reveals a very interesting fact. The numbers which express the ratios in which two elements combine with a fixed weight of *hydrogen* also express the ratio in which they combine with *each other*. Thus:

7.94 g. of oxygen combines with 19.88 g. of calcium
2 × 7.94 g. of oxygen combines with 16 g. of sulfur
19.88 g. of calcium combines with 16 g. of sulfur.

It is possible, therefore, *to assign to each element a number* which will express the relative weight by which it enters into combination with other elements. These numbers are called the *combining weights* of the elements. In Fig. 38 the lines connecting any two symbols at once indicate the ratio by weight in which the elements combine.

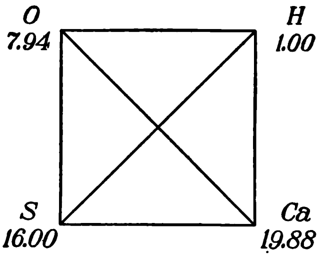


FIG. 38. Diagram showing the combining ratios of oxygen, hydrogen, sulfur, and calcium

Elements with more than one combining weight. It is evident that some elements have more than one combining weight, for we have seen that 1 part of hydrogen combines either with 7.94 or with 15.88 parts of oxygen. *In all such cases the number expressing the larger combining weight is a simple multiple of the number expressing the smaller one.*

Standard for combining weights. The combining weights are all *relative* to some one chosen standard. It is therefore possible to select any element as the standard, and any desired weight of that element as a unit for comparison. For many reasons it is better to select oxygen rather than hydrogen as the standard element. It is likewise better to select 8 g. rather than 1 g. as its standard value, so that no other element may have a combining weight of less than unity. If oxygen is taken as 8, hydrogen becomes 1.008; calcium, 20.07; and sulfur, 16.03.

The law of combining weights. The law of combining weights may now be stated as follows: *To each element may be assigned a number which in itself, or when multiplied by some integer, expresses the weight by which the element combines with other elements.*

Natural laws. In science a *law* is simply a statement of what might be called a *habit of nature.* The four laws mentioned at the beginning of the chapter are merely brief descriptions of how nature has been found to act in the matter of chemical combination. They do not explain anything; neither do they compel chemical action to take place in this way.

Theories. Having formulated a number of laws such as these, we can hardly help wondering why nature should act in so curious and interesting a fashion, and we set ourselves to imagine how matter *might* be made up so that these very laws would be a necessary result. We call this process of mind *forming a theory.*

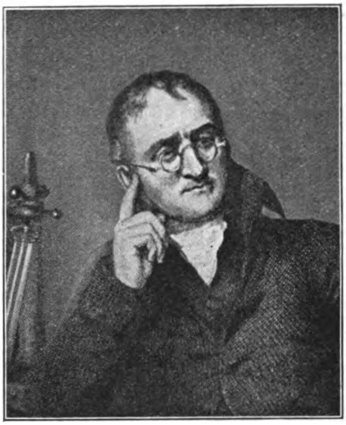


FIG. 39. John Dalton (English) (1766–1844)

The founder of the atomic theory

The atomic theory. Of all the theories that have been advanced concerning the nature of matter, the one proposed by John Dalton (Fig. 39), and known as the *atomic theory*, is the most satisfactory. The main points of this theory in its present form, together with the reasons for making them a part of the theory, are as follows:

1. Every weighable quantity of an elementary substance is made up of a very great number of unit bodies called *atoms.*

2. Experiment shows that the composition of a given compound is always the same. The simplest way to adjust the theory to this fact is to assume that the atoms of each

element all have the *same* weight, while those of different elements have *different* weights, and that during chemical union a definite number of one kind of atoms combines with a definite number of another kind to form a particle of a compound. If this should be true, a given compound would of necessity have a perfectly definite composition.

3. Since there is no change in weight when two substances act upon each other, it must be true that the weights of the individual atoms are unchanged as a result of the action.

4. To account for the law of multiple proportion we must assume that the atoms of two different elements may unite in different ratios; for example, if one atom of *A* unites with one of *B* under one set of conditions, but with two of *B* under other conditions, then we shall have two different compounds. The masses of *B* combined with a fixed mass of *A* will be in the ratio of 1 : 2, since the number of atoms are in this ratio.

5. The law of combining weights tells us that a definite number can be assigned to each element, which expresses its combining value. If each atom has its own peculiar weight, and if atoms always combine with each other in definite numbers, then these combining numbers indicate the *relative weights of the atoms themselves.* That an element may have two different combining weights, one a multiple of the other, is provided for by the supposition that the atoms are able to combine in several different ratios.

Summary of the atomic theory. The atomic theory suggests that all matter is made up of minute bodies called atoms. The atoms of a given element are all alike in weight, but those of different elements have different weights. When elements act upon each other, the action takes place between definite small numbers of the atoms.

Molecules and atoms. Dalton applied the name *atom* to both elements and compounds. It is evident, however, that the smallest particle of a compound must consist of at least two different kinds of atoms. The term *molecule* is now applied to the smallest particle which, taken in large numbers, makes up the bodies we deal with; for example, gases are made up of molecules which are moving about with great velocity. The term *atom* is applied to the smallest unit of an element which takes part in a chemical action.

Molecules of elements. Since two kinds of atoms unite to form a molecule of a compound, the question naturally arises, May not two or more atoms of the same kind combine to form a molecule of an elementary substance? It has been found that the elements differ among themselves in this respect. In some cases the atoms do not unite; in other cases, as with oxygen and hydrogen, two atoms unite to form a molecule of the element. The molecule of ozone contains three atoms. The experiments which prove that this is true will be described later (p. 189).

Value of a theory. The value of a theory is twofold: it makes the processes of nature more vivid to us, because it presents them as a picture rather than as abstract laws; it also leads to new discoveries. In adapting itself to known facts and laws almost any good theory will suggest a number of consequences which have not been observed, and experiments can then be made to see whether these are really as the theory predicts. Thus, the atomic theory predicted many properties of gases which have since been verified.

Sometimes the progress of discovery will show that a theory unquestionably expresses the truth, and the theory then becomes a statement of facts. There is so much evidence, drawn from so many sources, to show that the atomic theory expresses the facts about the constitution of matter, that there is little doubt as to the reality of atoms and molecules.

Atomic weights. It would be of great interest if we could determine the weights of the various kinds of atoms. They are so very small, however, that we can never hope to determine their weight even approximately. It has been shown that the smallest particle visible with the most powerful microscope ever constructed contains at least 1000 atoms.

We have seen, however, that the ratio between the combining weights is the same as between the weights of the atoms themselves, so that we should be able to determine their *relative* weights with precision. But most of the elements have more than one combining weight, and we must find some means of choosing the one which correctly expresses the weight of a single atom.

It has been found that, before this problem can be solved, methods must be devised for finding the relative weights of *molecules of compounds.* Such methods have been developed and will be described later on (Chap. XX). These methods have led to the adoption of a single number for each element, called its *atomic weight.* A list of atomic weights will be found on the back cover of the book. In every case they are either the smallest combining weight or some multiple of it.

EXERCISES

1. What other scientific laws can you think of besides the ones mentioned at the beginning of this chapter?

2. Suppose the combining weight of oxygen had been chosen as 100 instead of 8; what would then be the combining weight of hydrogen? *Ans.* 12.6.

TOPICS FOR THEMES

John Dalton (see encyclopedia).

The atoms of the Greek philosophers and the atom of Dalton (see encyclopedia).

CHAPTER IX

FORMULAS; EQUATIONS; CALCULATIONS

Percentage composition. Just as we can determine the composition of water with great accuracy (p. 46), so, by similar means, we can determine the composition of other compounds. Having analyzed a given compound, we usually express its composition in percentages, or in the parts of each element in 100 parts of the compound. Thus, we have seen that water consists of 88.81 per cent of oxygen and 11.19 per cent of hydrogen. This mode of expression takes no account of the fact that compounds are made up of molecules, the atoms of which each have characteristic weights. It would be much better to have a method of stating composition which would express all these facts.

Atomic composition. Remembering that the atomic weight of oxygen is 16, it is evident that if we divide the percentage of oxygen in water by 16, the quotient (5.55) will be the relative number of oxygen atoms in 100 parts of water. In like manner, if we divide the percentage of hydrogen (11.19) by the atomic weight of the element (1.008), the quotient (11.10) will express the relative number of hydrogen atoms in 100 parts of water. The two numbers, 5.55 and 11.10, therefore represent the *ratio between the number of oxygen and hydrogen atoms* in 100 g. of water. But this same ratio must hold for any other quantity of water, even for one molecule, since any quantity of water is made up of molecules. To reduce the ratio to its simplest terms we divide the two numbers by the smaller one:

$$5.55 \div 5.55 = 1; \quad 11.10 \div 5.55 = 2$$

The ratio of oxygen atoms to hydrogen atoms in a molecule of water is therefore 1 : 2.

Formulas. We may express the ratio found for the oxygen and hydrogen atoms in a molecule of water by writing the two symbols together thus, H_2O, the subscript 2 indicating that two atoms of hydrogen are in combination with one of oxygen. This is known as the *formula* of water.

Formula of potassium chlorate. In like manner we have found that potassium chlorate consists of 31.9 per cent potassium, 28.9 per cent chlorine, and 39.2 per cent oxygen.

$31.9 \div 39.2 = 0.8161$ = atomic weights of potassium in 100 g. potassium chlorate

$28.92 \div 35.45 = 0.8159$ = atomic weights of chlorine in 100 g. potassium chlorate

$39.16 \div 16 = 2.447$ = atomic weights of oxygen in 100 g. potassium chlorate

Dividing the three quotients by the smallest (0.8159), we get the integers 1, 1, 3. The formula of potassium chlorate is therefore $KClO_3$. Since analyses are always slightly inaccurate, the atomic ratios will usually differ slightly from integers, but there will be no doubt as to what the integer should be in a given case.

Facts expressed by formulas. Formulas are used to express several distinct facts:

1. ***Atomic composition of molecules.*** A formula shows the number and kinds of atoms in a molecule of a compound. The formula H_2O states that a molecule of water is composed of two atoms of hydrogen and one of oxygen. The formula of sulfuric acid, H_2SO_4, shows that its molecule consists of two atoms of hydrogen, one of sulfur, and four of oxygen.

2. ***Molecular weights of compounds.*** Since each atom has its own weight, the sum of all the atoms in a molecule must be the weight of the molecule itself relative to oxygen taken as 16. The relative weight of the molecule of water is therefore $(2 \times 1.008) + 16 = 18.016$. The relative weight of the molecule of sulfuric acid is $(2 \times 1.008) + 32.06 + (4 \times 16) = 98.076$.

3. ***Percentage composition of compounds.*** From the formula of a compound we can easily go back to the percentages from which it was calculated. Thus, if the molecule of water weighs 18.016 and contains one oxygen atom of weight 16, the fraction of its weight due to oxygen is $\frac{16}{18.016}$, or 88.81 per cent. The fraction due to hydrogen is $\frac{2.016}{18.016} = 11.19$ per cent.

The molecule of sulfuric acid weighs 98.076. Of this, $\frac{2.016}{98.076}$ (or 2.05 per cent) is hydrogen, $\frac{32.06}{98.076}$ (or 32.70 per cent) is sulfur, and $\frac{64}{98.076}$ (or 65.25 per cent) is oxygen.

Gram-molecular weights; formula weights. For practical purposes we deal with pounds or with grams of a substance, not with atoms and molecules. Now, since the numbers 18.016, 16, and 2.016 represent the ratio by weight between a molecule of water and the oxygen and hydrogen of which it is composed, the same ratios must hold between any weight of water we may choose and the oxygen and hydrogen in this weight of water. Evidently, in 18.916 lb. of water there will be 16 lb. of oxygen and 2.016 lb. of hydrogen, and in 18.016 g. there will be 16 g. of oxygen and 2.016 g. of hydrogen.

For practical purposes, therefore, we may allow the symbol H to stand for 1.008 g. of hydrogen, the symbol O for 16 g. of oxygen, and the formula H_2O for 18.016 g. of water. The weight in grams of an element, corresponding to its atomic weight, is called a *gram-atomic* or *symbol weight*. The weight in grams of a compound, corresponding to its molecular weight, is called a *gram-molecular weight* or *formula weight*.

Equations. Having devised a convenient way of expressing the composition of compounds, not in percentages but in formulas, we make use of *equations* to express chemical transformations, using an arrow in place of an equality sign. For example, the equation

$$2\,H + O \longrightarrow H_2O \qquad (1)$$

is a concise method of stating two distinct facts.

1. *Qualitatively*, it states that water is formed by the union of hydrogen and oxygen.

2. *Quantitatively*, it tells us that 2 symbol weights of hydrogen (2.016 g.) combine with 1 symbol weight of oxygen (16 g.) to form a formula weight of water (18.016 g.).

Molecular equations. Since a formula expresses the composition of a molecule, and since experiment has shown that a molecule of oxygen and one of hydrogen each contain two atoms, the formulas of these gases are written O_2 and H_2 rather than $2\,O$ or $2\,H$, which would simply represent two atoms not combined. If we wish our equation to state these additional facts, we shall have to change it to the form

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O \qquad (2)$$

This is called a *molecular equation*, and it will be seen that it expresses the same ratios by weight as does equation (1). It also expresses the fact that 2 molecules of hydrogen combine with 1 molecule of oxygen to form 2 molecules of water, and this makes it a more useful equation.

Decomposition of potassium chlorate. Let us take another example. It will be remembered that oxygen was prepared by heating potassium chlorate, which has the formula $KClO_3$. When heated, this compound decomposes into oxygen and a compound called potassium chloride, whose formula is KCl. The decomposition is represented by the equation

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

This equation states the following facts:

1. *Qualitatively*, potassium chlorate decomposes into potassium chloride and oxygen.

2. *Quantitatively*, 2 formula weights of potassium chlorate (2 × 122.6 g.) decompose into 2 formula weights of potassium chloride (2 × 74.69 g.) and 3 formula weights of oxygen (3 × 32 g.). The coefficient before a formula applies to the formula as a whole, while the subscript number applies only to the symbol which it follows.

3. *Molecularly*, 2 molecules of potassium chlorate decompose into 2 molecules of potassium chloride and 3 of oxygen.

Equations of reactions so far studied. Let us now put into the form of equations a number of the reactions studied up to this point, remembering that all of these equations rest upon careful experimental analysis.

1. ***Burning of mercury:***

$$2\,Hg + O_2 \longrightarrow 2\,HgO.$$

2. ***Preparation of oxygen:***

From mercuric oxide:

$$2\,HgO \longrightarrow 2\,Hg + O_2$$

From potassium chlorate:

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

From the electrolysis of water:

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

3. ***Preparation of hydrogen:***

From sodium and water:

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

From zinc and sulfuric acid:

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

From steam and iron:

$$3\,Fe + 4\,H_2O \longrightarrow Fe_3O_4 + 4\,H_2$$

4. ***Preparation of hydrogen peroxide:***

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

5. ***Preparation of ozone:***

$$3\,O_2 \longrightarrow 2\,O_3$$

Representation of the heat of reaction. We can also employ chemical equations to express the heat given off or absorbed during chemical action. The equation

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O + 136{,}800 \text{ cal.}$$

states the fact that when 4.032 g. of hydrogen combines with 32 g. of oxygen, forming 36.032 g. of water, heat is given off to the extent of 138,000 cal. Evidently, when 1 formula weight (18.016 g.) of water is formed, 69,000 cal. is given off, and this is called the *heat of formation* of water.

Conditions of a reaction not indicated by equations. Equations merely state the composition of the substances taking part in the reaction and the weights of each one involved, together with the energy change measured as heat. They do not tell the conditions under which the reaction will take place. For example, the equation

$$2\,HgO \longrightarrow 2\,Hg + O_2$$

does not tell us that it is necessary to keep heating the mercuric oxide to a moderately high temperature in order to effect its decomposition. The equation

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

in no way indicates that the hydrogen sulfate must be dissolved in water before it will act upon zinc. The equation

$$S + O_2 \longrightarrow SO_2$$

does not indicate that no perceptible action takes place unless the sulfur is first heated, but that when once started it goes on of its own accord and with a bright flame.

It will therefore be necessary to pay close attention to the details of the conditions under which a given reaction occurs, as well as to the statement of the equation itself.

Problems based on equations. Since an equation is a statement of the weights of materials which take part in a reaction, when the equation has once been established by experiment we can use it in calculating the various weights. A few examples will show how this may be done.

1. How many grams of oxygen are evolved on heating 100 g. of mercuric oxide?

First write the equation for the reaction involved:

$$2\,HgO \longrightarrow 2\,Hg + O_2 \qquad (1)$$

Next determine the relative weights of the amounts of the different substances involved in the reaction. The atomic weights of mercury and oxygen are respectively 200.6 and 16 (see table on back cover). Hence the relative weight of the 2 HgO equals 2(200.6 + 16), or 433.2. Similarly, the relative weight of the oxygen evolved, namely, O_2, equals 2 × 16, or 32. It is convenient now to write these numbers under the formulas in equation (1). This then becomes

$$\underset{433.2}{2\,HgO} \longrightarrow 2\,Hg + \underset{32}{O_2}$$

These numbers indicate that 433.2 units by weight (in this case grams) of mercuric oxide will, on heating, evolve 32 units by weight of oxygen; hence 1 g. of mercuric oxide will give $\frac{32}{433.2}$ g. of oxygen, and 100 g. will give $100 \times \frac{32}{433.2}$, or 7.38 g.; or the relation between the weights of the substances involved may be stated in the form of a proportion:

$$433.2 : 32 :: 100 : x$$
$$433.2\,x = 3200$$
$$x = 7.38$$

2. I wish to prepare 100 g. of oxygen, using potassium chlorate as a source of the oxygen. How many grams of the chlorate will be required?

$$\underset{245.12}{2\,KClO_3} \longrightarrow 2\,KCl + \underset{96}{3\,O_2}$$

Proportion: $245.12 : 96 :: x : 100$; or $x = 255.33$ g., *Ans.*

3. How many grams of zinc must be dissolved in sulfuric acid to produce 10 g. of hydrogen?

$$\underset{65.37}{Zn} + H_2SO_4 \longrightarrow ZnSO_4 + \underset{2.016}{H_2}$$

Proportion: $65.37 : 2.016 :: x : 10$; or $x = 324.2$ g., *Ans.*

It must be remembered that the equations show relations by *weight*, not by volume; hence in problems involving volumes of gases it will be necessary to first find the weights of the gases. The table in the Appendix gives the weight of 1 liter of each of the common gases, measured under standard conditions. The following problem will illustrate the method:

4. How many grams of potassium chlorate are necessary to prepare 100 liters of oxygen?

Since 1 liter of oxygen weighs 1.429 g., 100 liters will weigh 142.9 g.

$$\underset{245.12}{2\,KClO_3} \longrightarrow 2\,KCl + \underset{96}{3\,O_2}$$

Proportion: $245.12 : 96 :: x : 142.9$; or $x = 363.8$ g., *Ans.*

Suggestions. In working such problems, do not carry divisions beyond the second decimal place. If the third figure would be above 5, add 1 to the second decimal figure. Having completed such a problem, look to see if the result is reasonable.

EXERCISES

1. State all the facts expressed by the formulas HCl; HNO_3; $Ca(OH)_2$; H_3PO_4.

2. State all that is implied in the equation

$$3\,O_2 \longrightarrow 2\,O_3 - 64{,}800 \text{ cal.}$$

3. From the following analyses calculate the simplest formula:

(1)	S = 39.07%	O = 58.49%	H = 2.44%	*Ans.* H_2SO_3
(2)	Ca = 29.40%	S = 23.56%	O = 47.04%	*Ans.* $CaSO_4$
(3)	K = 38.67%	N = 13.88%	O = 47.45%	*Ans.* KNO_3

4. It is required to prepare 30 g. of oxygen by heating mercuric oxide. How much oxide must be heated? *Ans.* 406.13 g.

5. What weight of oxygen can be obtained by heating 100 g. of potassium chlorate? *Ans.* 39.17 g. What volume will this occupy under standard conditions? *Ans.* 27.41 liters.

6. What weight of hydrogen will be obtained by acting upon 100 g. of zinc with sulfuric acid? *Ans.* 3.08 g. What will be its volume under standard conditions? *Ans.* 34.3 liters.

7. A given volume of oxygen standing over water at 20° and 745 mm. measures 10 liters. What would be its volume under standard conditions? *Ans.* 8.92 liters. What is its weight? *Ans.* 12.75 g.

8. In making 15 liters (standard) of hydrogen from zinc and sulfuric acid, what weight of zinc sulfate would be formed? *Ans.* 19.8 g.

CHAPTER X

NITROGEN AND THE RARE ELEMENTS: ARGON, HELIUM, NEON, KRYPTON, XENON

Historical. Nitrogen was discovered by the Scottish chemist Rutherford in 1772. A little later the Swedish chemist Scheele (Fig. 40) showed it to be a constituent of air, and Lavoisier gave it the name *azote*, which means that it will not support life. The name *nitrogen* was afterwards given it because of its presence in niter.

FIG. 40. Karl Wilhelm Scheele (1735–1784)

A famous Swedish chemist

Occurrence. Dry air is composed principally of oxygen and nitrogen in the free state, about 78 parts out of every 100 parts by volume being nitrogen. Nitrogen also occurs in nature in the form of potassium nitrate (KNO_3) (commonly called saltpeter or niter), as well as in sodium nitrate ($NaNO_3$). It is also an essential constituent of all living organisms (refer to table, p. 10).

Preparation. Nitrogen can be readily obtained either from air or by decomposition of compounds containing the element.

1. ***Preparation from air.*** Nitrogen differs from oxygen in that it does not combine very readily with most elements save at very high temperatures. This suggests a convenient method for preparing it from air. It is only necessary to act upon a confined quantity of air with some substance which combines with the oxygen but which has no effect upon the nitrogen. The substances ordinarily used for this purpose are either phosphorus or copper. These are chosen not only because they combine readily with oxygen but because the oxides formed are solids, and on this account can be separated from the residue of nitrogen without difficulty. The nitrogen obtained in these ways is never quite pure, but contains about 1 per cent of a mixture of gases (chiefly argon) present in the air. These, however, do not materially affect the properties of the nitrogen.

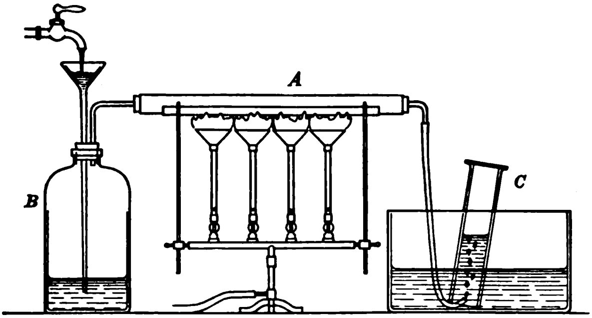


FIG. 41. The preparation of nitrogen by the action of copper upon air

Details of preparation of nitrogen. The method used for preparing nitrogen from the air by burning out the oxygen with phosphorus has already been described (p. 3).

When copper is used, the metal is placed in a tube *A* (Fig. 41) and heated. Air is then forced slowly through the tube by pouring water into the bottle *B*. The oxygen of the air combines with the hot copper, forming the black solid, copper oxide (CuO), which remains in the tube, while the nitrogen passes on and is collected over water in the cylinder *C*.

2. ***Preparation from compounds of nitrogen.*** Ammonium nitrite (NH_4NO_2) serves as a convenient source for preparing pure nitrogen. When the compound is heated, the change represented in the following equation takes place:

$$NH_4NO_2 \longrightarrow 2\,H_2O + N_2$$

Properties. Nitrogen is similar to oxygen and hydrogen in that it is a colorless, odorless, and tasteless gas. One liter of nitrogen weighs 1.2507 g. It is almost insoluble in water. It can be obtained in the form of a colorless liquid having a boiling point of −195.7°. At −210.5° it solidifies.

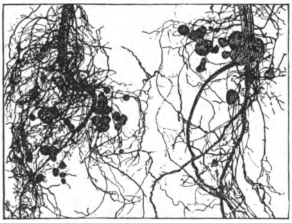


FIG. 42. Tubercles on the roots of bean plants

Chemical conduct. Under ordinary conditions nitrogen is very inactive. It does not easily combine with oxygen, as is evident from the fact that the air contains both of these gases; nor does it combine with anything else very readily, as is apparent from the fact that there is so much of it in the air and so little in the earth's crust in combination with other elements.

At high temperatures the activity of nitrogen greatly increases. When it is mixed with oxygen and strongly heated, a small fraction of the two gases combine, but the action is always very incomplete. The best results are obtained by passing electric sparks through a mixture of the two gases (or air) or by causing the mixture to flow through an electric arc. Under these conditions nitric oxide (NO) forms.

Under similar conditions nitrogen and hydrogen combine to a limited extent to form the hydride, ammonia (NH_3). When nitrogen is heated with metals, the action is much more energetic, particularly with magnesium, titanium, or aluminium. The resulting compounds are called *nitrides*, just as compounds of an element with oxygen are called *oxides*.

The assimilation of nitrogen by plants. While nitrogen is an essential constituent of both plants and animals, yet with the exception of a few plants none of these organisms have the power of directly assimilating free nitrogen. For example, the nitrogen in our bodies is taken from our foods and not from the air which we inhale. It has long been known, however, that certain plants, chiefly clover, alfalfa, beans, and similar plants belonging to the natural order *Leguminosae*, not only thrive in poor soil but at the same time enrich it. It is now known that these plants obtain at least a portion of their nitrogen from the atmosphere. This is accomplished by groups of microörganisms which are gathered in little tubercles on the roots of the plants (Fig. 42). These organisms convert the nitrogen of the air into compounds of nitrogen; some of these are assimilated by the plant and some are left in the soil and thus enrich it.

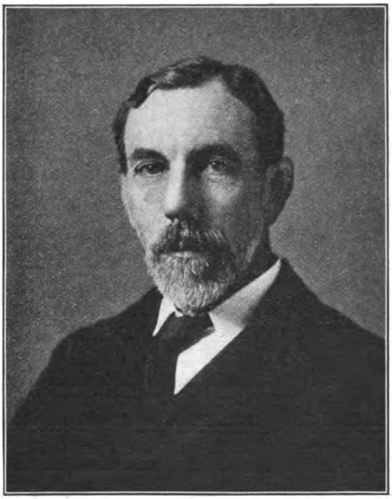


FIG. 43. Sir William Ramsay (1852–)

The discoverer of the rare elements present in the atmosphere

Argon, helium, neon, krypton, xenon. These are rare elements and occur in the air in very small quantities. They are similar in that they are all colorless, odorless gases. They differ from all other known elements in that they are entirely inert, forming no compounds whatever. Argon, the most abundant of the group, was discovered in 1894 by two British scientists, Lord Rayleigh and Sir William Ramsay (Fig. 43). In 1868 Lockyer showed that a gaseous element, to which he gave the name *helium*, was present in the gases surrounding the sun. In 1895 Ramsay showed that this same element was present in the gases evolved in heating certain minerals, and later that traces of it were present in the atmosphere. The three remaining members of the group were discovered by Ramsay and Travers in 1898. They obtained them from liquid air, thus proving their presence in the atmosphere.

Helium is of interest in that, of all known gases, it is the most difficult to liquefy. It was first obtained in liquid form in 1908. The boiling point of the liquid is – 268.7°. Some facts pertaining to these gases are given in the following table:

TABLE OF RARE ATMOSPHERIC ELEMENTS

	Helium	Neon	Argon	Krypton	Xenon
Weight of 1 liter . .	0.1782 g.	0.9002 g.	1.7809 g.	3.708 g.	5.851 g.
Boiling point of liquid form	– 268.7°	– 239°	– 186°	– 151.7°	– 109°
Number of volumes in 1,000,000 volumes of air (approximate) .	4.00	12.3	9400	0.05	0.006

EXERCISES

1. Why not prepare nitrogen by burning a candle in confined air?

2. In Fig. 4 why does the withdrawal of oxygen cause the water to rise in the bell jar?

3. Which contains the greater percentage of nitrogen: sodium nitrate or potassium nitrate?

4. 100 liters of dry air contain how many liters of nitrogen? What is the weight of this volume of nitrogen? *Ans.* 97.55 g.

5. What weight of ammonium nitrite will be required for the preparation of 10 g. of nitrogen? *Ans.* 22.9 g. What will be the volume of the nitrogen under standard conditions? *Ans.* 8 liters.

6. A quantity of nitrogen standing over water at 20° and 750 mm. measured 25 liters. What will be the volume under standard conditions? *Ans.* 22.9 liters.

TOPICS FOR THEMES

Argon and the rare atmospheric gases (McPherson and Henderson, A Course in General Chemistry).

Fixation of nitrogen by plants (Duncan, Chemistry of Commerce; also write to the Department of Agriculture, Washington, D.C., for bulletins).

CHAPTER XI

THE ATMOSPHERE

Historical. The terms *atmosphere* and *air* are often used interchangeably, although strictly speaking the former term is applied to the entire gaseous envelope surrounding the earth, while the latter is applied to a limited portion of this envelope. Like water, air was formerly regarded as an element. Near the close of the eighteenth century, however, through the experiments of Scheele, Priestley, Cavendish, and Lavoisier, it was shown to be a mixture of at least two gases — those which we now call oxygen and nitrogen. By absorbing the oxygen from an inclosed volume of air and measuring the contraction in volume due to the removal of oxygen, Cavendish was able to determine with considerable accuracy the relative volumes of oxygen and nitrogen present.

Composition of the air. The normal constituents of air, together with the approximate volumes of each in samples collected in the open fields, are as follows:

Oxygen	21 volumes in 100 volumes of dry air
Nitrogen	78 volumes in 100 volumes of dry air
Water vapor	variable within wide limits
Carbon dioxide . . .	3 to 4 volumes in 10,000 volumes of dry air
Argon	0.940 volumes in 100 volumes of dry air
Helium, neon, krypton, xenon	traces

In addition there are usually present small quantities of hydrogen peroxide, ammonium nitrate, microörganisms, dust particles, and traces of hydrogen. Although not definitely proved, it is probable that small amounts of ozone are also present. The air in large cities and manufacturing districts is also likely to contain certain gases evolved in manufacturing processes. Among these are hydrogen sulfide (H_2S) and sulfur dioxide (SO_2).

Water vapor in the air. The quantity of water vapor which may be present in the air varies with the temperature. This is shown in the following table, which gives the weight in grams of the water vapor that 1 cu. m. of air can absorb at the temperature indicated:

Temperature,	0°	10°	20°	30°
Weight of water,	4.8 g.	9.9 g.	17.1 g.	30 g.

The constituents of the air that are essential to life. The constituents that are known to be essential to life are oxygen, nitrogen, water vapor, and carbon dioxide. The first three of these have already been discussed in detail. The remaining one, carbon dioxide, is a gas having the formula CO_2. It is evolved in the processes of both respiration and combustion (p. 20), so that large quantities of it are constantly being added to the atmosphere. The properties of the gas will be described in the chapter relating to the compounds of carbon; it is only necessary to note here that it is a comparatively heavy gas and will neither burn nor support combustion.

The oxygen in the atmosphere directly supports life through the process of respiration. The nitrogen serves to dilute the oxygen and thus to diminish the intensity of its action. It is likewise assimilated by certain plants (p. 83). The water vapor prevents excessive evaporation of the water present in organisms, while the carbon dioxide is an essential plant food.

The quantitative analysis of air. A number of different methods have been devised for the determination of the percentages of the constituents of the atmosphere. Among these are the following:

1. ***Determination of oxygen.*** The oxygen is withdrawn from a measured volume of air inclosed in a tube, by means of phosphorus.

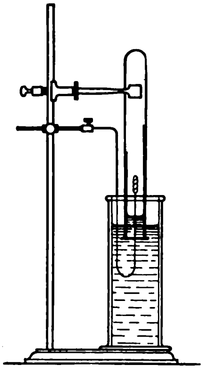


FIG. 44. The withdrawal of oxygen from a measured volume of air by phosphorus

To make the determination, a graduated tube is filled with water and inverted in a vessel of water. A sample of the air to be analyzed is then introduced into the tube until it is nearly filled with the gas, and the volume is carefully noted. A small piece of phosphorus is attached to a wire and brought within the tube as shown in Fig. 44. After a few hours the oxygen in the inclosed air will have combined with the phosphorus, the water rising to take its place. The phosphorus is removed, and the volume is again noted. The contraction in the volume of the air is equal to the volume of oxygen absorbed.

2. ***Determination of nitrogen.*** If the gas left after the removal of oxygen from a portion of air is passed over heated magnesium, the nitrogen is withdrawn, leaving argon and the other rare elements. It may thus be shown that, of the 79 volumes of gas left after the removal of the oxygen from 100 volumes of air, approximately 78 are nitrogen and 0.93 argon. The other elements are present in such small quantities that they may be neglected.

3. ***Determination of water vapor and carbon dioxide.*** These constituents are determined by passing a known volume of

air through two tubes, the first containing calcium chloride, and the second calcium hydroxide, or, better, sodium hydroxide. The calcium chloride removes the moisture, while the sodium hydroxide removes the carbon dioxide. The increase in the weights of these two substances will give the weights of moisture and carbon dioxide respectively in the original volume of air.

Processes tending to change the composition of the air. These processes naturally fall into two classes: those which increase the carbon dioxide and those which diminish it.

1. ***Processes tending to increase the quantity of carbon dioxide.*** Not only do large quantities of carbon dioxide escape into the atmosphere from volcanoes and crevices in the earth's crust, but certain processes are constantly taking place which are attended by evolution of this gas. Chief among these are the following: (a) *Respiration.* In this process some of the oxygen in the inhaled air is absorbed by the blood and carried to all parts of the body, where it combines with the carbon of the worn-out tissues. The products of oxidation are carried back to the lungs and exhaled largely in the form of carbon dioxide. (b) *Combustion.* All the ordinary fuels contain large percentages of carbon. On burning, this is oxidized to carbon dioxide. (c) *Decay of organic matter.* When organic matter decays in the air the carbon present is oxidized to carbon dioxide.

2. ***Processes tending to decrease the quantity of carbon dioxide.*** There are two general processes which tend to diminish the quantity of carbon dioxide in the atmosphere.

(a) *The action of plants.* Plants have the power, when growing in sunlight, of absorbing carbon dioxide from the air, retaining the carbon and returning a portion of the oxygen to the air. It is from this source that plants obtain their entire supply of carbon.

That plants evolve oxygen in the sunlight may be shown as follows: Some freshly gathered leaves are placed under water in the jar *A* (Fig. 45) and covered with the funnel *B*, the stem of which extends into the graduated tube *C*. Bubbles of oxygen make their escape from the surface of the leaves, and may be collected in the measuring tube *C*.

(b) *The weathering of rocks.* Large quantities of carbon dioxide are being constantly withdrawn from the atmosphere through its combination with various rock materials.

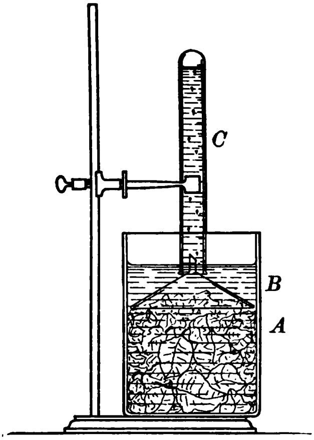


FIG. 45. The liberation of oxygen from plants exposed to sunlight

The composition of the air constant. Notwithstanding the changes constantly taking place which tend to alter the composition of the air, the results of a great many analyses of air collected in the open fields show that the percentages of oxygen and nitrogen, as well as of carbon dioxide, are very nearly constant. Indeed, so constant are the percentages of oxygen and nitrogen that the question has arisen, whether air is not a definite chemical compound.

Air a mixture. That the oxygen and nitrogen in the air are not combined may be shown in a number of ways, among which are the following:

1. When air dissolves in water it has been found that the ratio of oxygen to nitrogen in the dissolved air is no longer 21 : 78, but more nearly 35 : 65. If air were a chemical compound, the ratio of oxygen to nitrogen would not be changed by solution in water.

2. A chemical compound in the form of a liquid has a definite boiling point at a given pressure (p. 57). Water, for example, boils at 100° under standard pressure. Moreover, the steam which is formed has the same composition as the water. The boiling point of liquid air, on the other hand, gradually rises as the liquid boils, the nitrogen escaping first followed by the oxygen. If the two were combined, they would pass off together in the ratio in which they are found in the air.

Why the air has a constant composition. If air is a mixture and changes are constantly taking place which tend to modify its composition, how, then, do we account for the constancy of composition which the analyses reveal ? This is explained by several facts: (1) The changes which are caused by the processes of combustion, respiration, and decay, on the one hand, and the action of plants, on the other, tend to equalize each other. (2) The winds keep the air in constant motion and so prevent local changes. (3) The volume of air is so vast and the changes which occur are so small, compared with the total volume, that they cannot be readily detected. (4) Finally, it must be noted that only air collected in the open fields shows this constancy in composition. The air in a poorly ventilated room occupied by a number of people rapidly changes in composition.

Impure air and ventilation. The difference in the percentages of oxygen, carbon dioxide, and moisture present in inhaled and exhaled air are shown in the following table:

CONSTITUENT	INHALED AIR	EXHALED AIR
Oxygen	21.00%	16.00%
Carbon dioxide	0.04%	4.38%
Water vapor	variable	saturated

The injurious effects resulting from inadequate ventilation seem to be due neither to lack of oxygen nor to the excess of carbon dioxide; rather they are due to high temperature and to the presence of an abnormal amount of water vapor, both of which conditions are apt to prevail in crowded and poorly ventilated rooms.

Not only is water vapor exhaled from the lungs, but there is constant evaporation of moisture from the pores of the skin, and in this process much heat is absorbed. Notwithstanding the extreme changes in the temperature of the air, the temperature of the body in health remains nearly constant. It is partly by variations in the amount of moisture evaporating from the skin that the temperature of the body is maintained at this constant value. If an abnormal amount of water vapor is present in the air, the evaporation of moisture from the skin takes place very slowly, and bodily discomfort follows. Moreover, when the air is perfectly still, that portion of the air in contact with the body tends to become saturated with moisture, and evaporation diminishes; hence the relief that comes from keeping the air in motion, as with an electric fan.

In general, a moisture content of about 70 per cent of that required for saturation is most conducive to comfort. The volume of fresh air necessary for good ventilation varies greatly with conditions, but in general may be said to be about 30 cu. ft. per minute for each person present.

The properties of air. Inasmuch as air is composed principally of a mixture of oxygen and nitrogen, which elements have already been discussed, its properties may be inferred largely from those of the two gases. One liter weighs 1.2928 g.

Liquid air. Like all other gases, air can be liquefied and solidified by the combined effect of pressure and low temperature. Air is now liquefied on a commercial scale by compressing it by means of powerful pumps, the temperature of the compressed gas being lowered sufficiently by allowing a portion of the gas to expand in such a way that the heat absorbed in the expansion is largely withdrawn from the remaining gas.

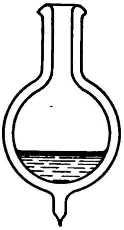


FIG. 46. A Dewar flask for preserving liquid air

Liquid air is essentially a mixture of liquid nitrogen (boiling point, – 195.7°) and liquid oxygen (boiling point, –182.9°); hence if liquid air is allowed to evaporate, the nitrogen tends to vaporize first. Advantage is taken of this difference in boiling points to separate the oxygen and nitrogen from each other, and the method serves as a commercial one for obtaining the two gases. Liquid air is also employed when very low temperatures are desired.

Dewar flasks; thermos bottles. Liquid air may be kept for some hours in a special form of flask devised by the Scottish scientist, Dewar, known as a *Dewar flask.* This consists of two concentric vessels (Fig. 46) of any convenient shape. These are joined together at the upper rim only, and the space between them is exhausted by an air pump. The vacuum serves as the best possible insulator to prevent heat conduction. The surface of the outer flask is often silvered, in order to reflect the external heat and thus prevent its absorption. The so-called *thermos bottles* (Fig. 47) are constructed on the same plan and are very effective for keeping liquids either hot or cold for several hours.

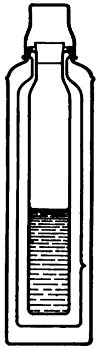


FIG. 47. A thermos bottle

Combustion in air and in oxygen. Knowing the composition of air and the properties of oxygen and nitrogen, one can readily understand why substances burn more readily in pure oxygen than in air. Since combustion consists in the union of matter with oxygen, it is evident that the speed of the action will be influenced by the amount of oxygen which is in contact with the burning body. When combustion takes place in air, only about one fifth as much oxygen can come in contact with the body as in pure oxygen, and the speed of the action is therefore correspondingly less. Moreover, the speed increases with the temperature. When a substance burns in air, much of the heat generated is spent in heating the nitrogen present. The temperature reached is therefore less, and the speed of the action is correspondingly slower.

Dust explosions. Experiments show that under proper conditions a combustible body floating in the air in the form of a powder will burn almost instantaneously when ignited, since the extent of surface exposed to the oxygen is very great. The result is an explosion. Flour-mills have been known to explode with great violence, and many of the most powerful mine explosions are due to the combustion of the coal dust floating in the air of the mine, which in some way becomes ignited.

EXERCISES

1. When oxygen and nitrogen are mixed in the proportion in which they exist in the atmosphere, heat is neither evolved nor absorbed by the process. What important point does this suggest?

2. How does the air in manufacturing districts differ in composition from that in the open fields?

3. Can you suggest any reason why the growth of clover in a field improves the soil?

4. When ice is placed in a vessel containing liquid air, the latter boils violently. Explain.

5. Does an electric fan lower the temperature of a room? of an individual in the room?

6. What is the meaning of the word *thermos*?

7. Assuming that dry wood contains 40 per cent carbon, all of which originally came from carbon dioxide in the air, what weight of CO_2 would have to be absorbed by a plant to make 500 g. of wood? *Ans.* 733.3 g. What volume would this occupy under standard conditions? *Ans.* 370.9 liters.

8. Taking the volumes of the oxygen and nitrogen in 100 volumes of air as 21 and 78 respectively, calculate the percentages of these elements present in the air by weight.

9. Would combustion be more intense in liquid than in gaseous air?

10. A tube containing calcium chloride was found to weigh 30.1293 g. A volume of air which weighed 15.2134 g. was passed through, after which the weight of the tube was found to be 30.3405 g. Find the percentage of moisture present in the air. *Ans.* 1.39 per cent.

Topics for Themes

The atmospheric conditions leading to fog, rain, snow, and hail.
Liquid air (see encyclopedia).

CHAPTER XII

SOLUTIONS AND IONIZATION

Definitions. When a solid is thoroughly stirred through a liquid the solid often passes completely from sight as an individual body, or *dissolves*, forming a *solution*. The liquid in which the substance dissolves is called the *solvent*, while the dissolved substance is the *solute*.

It often happens that the solid does not really dissolve but remains suspended in the liquid, rendering it cloudy. This is true of clay shaken with water. Upon standing quietly for some time, however, matter in suspension gradually settles, while matter in true solution does not. The rapidity of settling depends upon the size of the solid particles.

Saturated solutions. On adding a solid to a liquid in small portions at a time, it will be found that a point is reached at which the liquid will not, at that temperature, dissolve more of the solid; the solid and the solution remain apparently unchanged in contact with each other, the rate at which the solid dissolves being just balanced by the rate at which solid crystallizes out. This condition may be described by saying that solid and solution are in *equilibrium* with each other. A solution is said to be *saturated* at a given temperature when it remains unchanged in concentration in contact with some of the solid. The weight of the solid which will completely saturate a definite volume of a liquid at a given temperature is called the *solubility* of the substance at that temperature.

Supersaturated solutions. Most solids are more soluble in hot than in cold liquids, and a liquid, saturated at a high temperature, usually deposits the excess of solute in the form of crystals as the temperature falls, maintaining saturation at all temperatures. Sometimes the crystals fail to form as the solution cools, especially if it is not disturbed in any way. The solution then contains more of the solute than is normally present when the solution is in equilibrium with the solid. Such a solution is said to be *supersaturated.* When a crystal of the solid is added to the supersaturated solution the excess of solute at once crystallizes out, the crystallization starting from the added crystals. This may be shown in a striking way by suspending a small crystal by a thread in a supersaturated solution (Fig. 48). The crystal grows rapidly in size, and fragments, breaking off, start crystallization at other points.

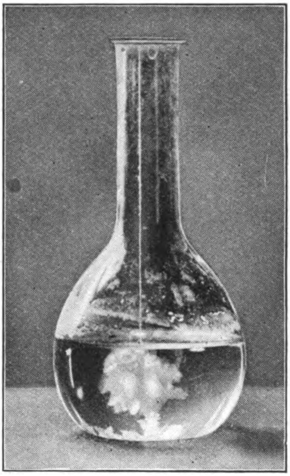


FIG. 48. The rapid growth of a crystal suspended in a supersaturated solution

Classes of solutions. All gases mix freely with each other in all proportions, and such mixtures may be regarded as the solution of one gas in another. Gases, liquids, and solids dissolve in liquids, and one solid frequently dissolves in another. The most familiar of these classes are solutions of gases or solids in liquids.

Conditions affecting solubility. A number of different conditions influence the solubility of a substance in a liquid.

1. ***Nature of the solute.*** Each substance has its peculiar solubility just as it has its own odor, taste, or crystalline form. All substances may be regarded as being soluble to

some extent in every liquid, but in many cases the solubility is so small that it cannot be measured. In other cases it is very great. Some solids dissolve in less than their own weight of water, and some gases, such as ammonia, dissolve to the extent of 1000 volumes in 1 volume of water.

2. ***Nature of the solvent.*** The nature of the solvent is no less important. Water, alcohol, and ether each have their own peculiar solvent power. Water is probably the most general solvent for all classes of materials, and alcohol is perhaps next to it. Ether, chloroform, and benzene are good solvents for organic substances such as fats, waxes, and oils.

3. ***Temperature.*** The weight of a solid which a given liquid can dissolve varies with the temperature. Usually it increases rapidly as the temperature rises, so that the boiling liquid dissolves several times the weight which the cold liquid will dissolve. In some instances, as in the case of the solubility of common salt in water, the temperature has little influence, and a few solids are more soluble in cold water than in hot.

In the case of gases, on the other hand, the lower the temperature of the liquid the larger the quantity of gas which it can dissolve. At 0°, 1000 volumes of water will dissolve 41.14 volumes of oxygen; at 50°, 18.37 volumes; at 100°, none at all. While most gases can be expelled from a liquid by boiling the solution, some cannot. For example, it is not possible by boiling to expel hydrogen chloride gas completely from its solution.

Tables of solubilities. For convenience of reference the facts known about the solubilities of various substances have been collected into *tables of solubilities*, and these are constantly used by the chemist. Tables giving the solubilities of a few of the most familiar substances will be found in the Appendix.

4. ***Pressure.*** Change of pressure has little effect upon the solubility of a solid, but greatly influences that of a gas. *The weight of a gas which dissolves in a given case is proportional to the pressure exerted upon the gas* (*Henry's law*). If the pressure is doubled, the weight of the gas going into solution is doubled; if the pressure is diminished one half, then but half as much gas will dissolve. Under high pressure large quantities of a gas can be dissolved in a liquid, and when the pressure is removed, the escape of the gas causes the liquid to foam, or *effervesce*, as in the familiar example of soda water.

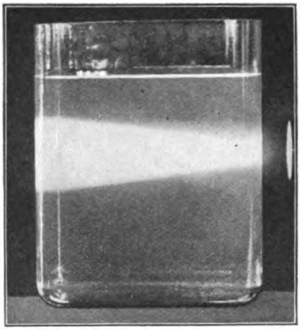


FIG. 49. A beam of light shining through a colloidal solution

Colloidal suspensions. In some cases a solid may be distributed through a liquid in so fine a state of division that it does not render the liquid noticeably cloudy, and does not settle out even after long standing; yet it does not form a true solution. This is called a *colloidal suspension*, or *colloidal solution*, and the solid forming it is called a *colloid.* Starch, gums, resins, gelatin, and glue are typical colloids.

That the material in a colloidal suspension is not really in solution is shown by the fact that a strong beam of light directed through such a suspension has a bright path, like a sunbeam in a dark, dusty room, while its path through a true solution is invisible. Fig. 49 is a photograph of a beam of light from a lantern, shining through a colloidal solution.

Emulsions. When two liquids which do not freely mix with each other, such as water and oil, are shaken violently together, a milky liquid results, consisting of very small droplets of the one liquid suspended in the other. As a rule the milkiness quickly disappears, the lighter liquid collecting as a layer on top of the heavier (Fig. 50, *A*). If a colloidal material, such as soap, is added before shaking, this separation is very slow, and the milky liquid is called an *emulsion* (Fig. 50, *B*). Milk is a typical emulsion, the butter fat being emulsified by the colloidal materials present in the milk.

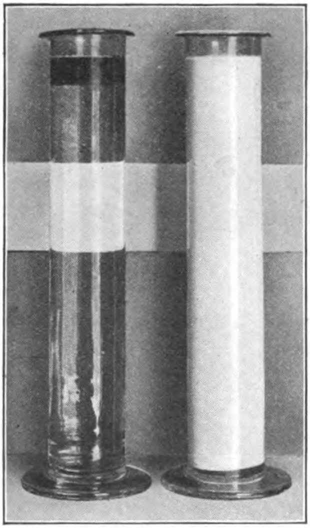


FIG. 50. Emulsions

In *A* the oil floats on the water. If soap is added and the mixture shaken, an *emulsion* is formed as shown in *B*

Characteristic properties of solutions. A few general statements may be made in reference to some characteristic properties of solutions.

1. ***Distribution of the solid in the liquid.*** A solid, when dissolved, tends to distribute itself uniformly through the liquid, so that every part of the solution has the same concentration. The process goes on very slowly unless hastened by stirring or shaking the solution. If a few crystals of a highly colored substance, such as potassium permanganate, are placed in the bottom of a tall vessel full of water, it will take weeks for the solution to become uniformly colored.

2. ***Boiling point of solutions.*** The boiling point of a liquid is raised by the presence of a substance dissolved in it. In general the extent to which the boiling point of a solvent is raised by a given substance is proportional to

the molecular concentration of the solution; that is, to the number of gram-molecular weights of the substance dissolved in a definite weight of the solvent.

3. ***Freezing point of solutions.*** The freezing point of a liquid is lowered by the presence of a substance dissolved in it. The lowering of the freezing point obeys a law similar to the one which holds for the raising of the boiling point, the extent of the lowering being proportional to the molecular concentration of the solution.

Electrolysis of solutions. Pure water does not appreciably conduct the electric current. If, however, certain substances, such as common salt or acids, are dissolved in the water, the resulting solutions are found to be good conductors and are called *electrolytes.* When the current passes through an electrolyte, some chemical change always takes place. This change is called *electrolysis.*

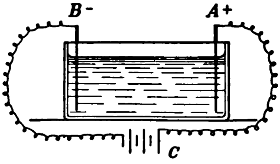


FIG. 51. The process of electrolysis

The general method used in the electrolysis of a solution is illustrated in Fig. 51. Two plates or rods, *A* and *B*, made of suitable material, are connected with the wires from a battery (or dynamo) *C* and dipped into the electrolyte, as shown in the figure. These plates or rods are called *electrodes.* The electrode *B* connected with the negative pole of the battery is the negative electrode, or *cathode*, while that connected with the positive pole *A* is the positive electrode, or *anode.*

Theory of ionization. The facts discovered in connection with electrolysis, together with many others, have led chemists to adopt a theory of solutions called the *theory of ionization.* This theory was first proposed by the Swedish chemist Arrhenius (Fig. 52). Its main points are as follows:

1. ***Formation of ions.*** The molecules of many compounds, when dissolved in water, fall apart, or *dissociate*, into two or more parts, called *ions*. Thus, sodium nitrate ($NaNO_3$) dissociates into the ions Na and NO_3; sodium chloride (NaCl), into the ions Na and Cl. These ions move about in the solution independently of each other like independent molecules, and for this reason were given the name *ion*, which means "wanderer."

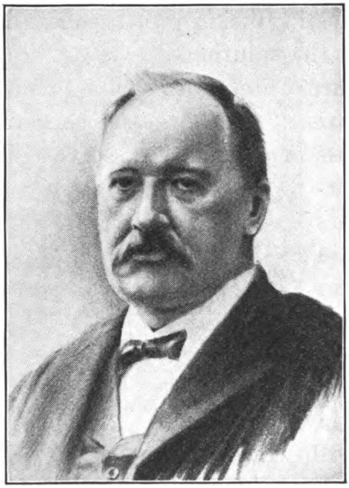


FIG. 52. Svante August Arrhenius (1859–)

A Swedish chemist, who suggested the theory of ionization

2. ***The electrical charge of ions.*** An ion differs from an atom or molecule in that it carries a large electrical charge. It is evident that the sodium ion must differ in some important way from ordinary sodium, for sodium ions, formed from ordinary salt, give no visible evidence of their presence in water, whereas metallic sodium at once decomposes the water. The electrical charge, therefore, greatly modifies the usual chemical properties of the element.

3. ***The positive charges equal the negative charges.*** The ions formed by the dissociation of any molecule are of two kinds: one is charged with positive electricity and the other with negative. The sum of all the positive charges is always equal to the sum of all the negative charges, and the solution as a whole is therefore electrically neutral. If we represent ionization by the usual chemical equations, with

the electrical charges indicated by plus (+) and minus (−) signs following the symbols, the ionization of sodium chloride molecules is represented thus:

$$NaCl \longrightarrow Na^+ + Cl^-$$

Those ions that are positively charged are known as *cations*, while those that are negatively charged are termed *anions*.

4. ***Not all compounds ionize.*** It is assumed that only those compounds ionize whose solutions are electrolytes. Thus, salt ionizes when dissolved in water, for it has been found that the resulting solution is a very good electrolyte. Sugar, on the other hand, does not ionize, and its solution is not a conductor of the electric current.

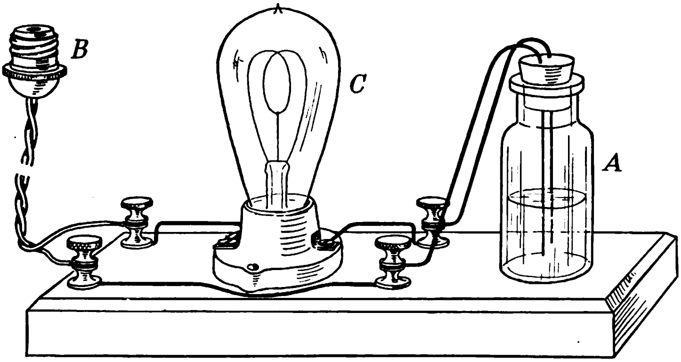


FIG. 53. Laboratory method for showing whether or not a solution is a conductor

Fig. 53 illustrates a very convenient apparatus for determining whether a solution is a good conductor. The solution is placed in the bottle *A* and the electrodes are dipped into it. Connection with the lighting circuit is made by the cord and plug *B*. If the solution is a good conductor, the current will flow through the lamp *C*, which will then glow.

The theory of ionization and the properties of solutions. In order to be of value, this theory must be in accord with the chief properties of solutions. Let us now see if the theory is in harmony with certain of these properties.

The theory of ionization and the boiling and freezing points of solutions. We have seen that the boiling point of a solution of a substance is raised in proportion to the number of molecules of the solute present in the solution.

It has been found, however, that *in the case of electrolytes* the boiling point is raised *more* than it should be to conform to this law. If the solute dissociates into ions, the reason for this becomes clear. Each ion has the same effect on the boiling point that a molecule has, and since their number is always greater than the number of molecules from which they were formed, the effect on the boiling point is abnormally great.

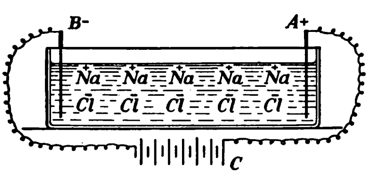


FIG. 54. The electrolysis of sodium chloride

In a similar way the theory furnishes an explanation of the abnormal lowering of the freezing point of electrolytes.

The theory of ionization and electrolysis. The changes taking place during electrolysis harmonize very completely with the theory of ionization. This will become clear from a study of the following examples:

1. ***Electrolysis of sodium chloride.*** Fig. 54 represents a vessel in which the electrolyte is a solution of sodium chloride (NaCl). According to the theory of ionization, the molecules of sodium chloride dissociate into the ions Na^+ and Cl^-. Since the cathode *B* has a large negative charge derived from the battery *C*, the Na^+ ions are attracted to it. On coming in contact with the cathode, they give up

their positive charge and are then ordinary sodium atoms. They immediately decompose the water according to the equation

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

and hydrogen gas is evolved from the surface of the cathode.

In a similar way the chlorine ions (Cl^-) are attracted to the positively charged anode *A*, and upon giving up their charge to it they are set free as chlorine atoms and may either combine with each other to form molecules of chlorine gas, or may attack the water as represented in the equation

$$4\,Cl + 2\,H_2O \longrightarrow 4\,HCl + O_2$$

It is to be carefully noted that the current does not bring about the decomposition of the solute into ions, but that it can pass through the solution only when ions are already present.

2. ***Electrolysis of water.*** The reason for the addition of sulfuric acid to water in the preparation of oxygen and hydrogen by electrolysis (p. 17) can now be made clear. Water itself is not an electrolyte to an appreciable extent, for it does not form enough ions to carry a current. Sulfuric acid (H_2SO_4) dissolved in water is an electrolyte, and dissociates into the ions $2\,H^+$ and SO_4^{--}, each SO_4^{--} ion having two negative charges. In the process of electrolysis of the solution the H^+ ions travel to the cathode, and on being discharged, escape as hydrogen gas. The SO_4^{--} ions, when discharged at the anode, act upon the water, setting free oxygen and once more forming sulfuric acid:

$$2\,SO_4 + 2\,H_2O \longrightarrow 2\,H_2SO_4 + O_2$$

The sulfuric acid can again ionize and the process repeat itself as long as any water is left. Hence the hydrogen and oxygen set free in the electrolysis of water really come *directly* from the acid but *indirectly* from the water.

Properties of electrolytes dependent upon the ions present. When a substance capable of forming ions is dissolved in water, the properties of the solution will depend upon two factors: (1) the ions formed from the substance; (2) the undissociated molecules. Since the ions are usually more active chemically than the molecules, most of the chemical properties of an electrolyte are due to the ions rather than to the molecules.

The solutions of any two substances which give the same ion will have certain properties in common. Thus, all solutions containing the copper ion Cu^{++} are blue, unless the color is modified by the presence of ions or molecules having some other color.

EXERCISES

1. Why does the water from some natural springs effervesce?

2. Why does not the water of the ocean freeze?

3. Why does shaking or stirring make a solid dissolve more rapidly in a liquid?

4. Why will vegetables cook faster when boiled in strong salt water than when boiled in soft water?

5. How do you explain the foaming of soda water?

6. Account for the fact that sugar sometimes deposits from sirups, even when no evaporation has taken place.

7. How did the ocean become salty?

8. What is the solubility of CO_2 in water (see Appendix)? On drawing a liter of soda water from a fountain, 500 cc. of CO_2 escaped. Assuming that the temperature was 0°, what was the pressure upon the gas in the fountain? *Ans.* 1.29 atmospheres.

9. 10 g. of common salt was dissolved in water and the solution evaporated to dryness; what weight of solid was left? *Ans.* 10 g. 10 g. of zinc was dissolved in hydrochloric acid and the solution evaporated to dryness; what weight of solid was left? *Ans.* 20.8 g.

TOPIC FOR THEMES

Describe the details of a soda-water fountain (from examination).

CHAPTER XIII

ACIDS, BASES, AND SALTS; NEUTRALIZATION

Acids, bases, and salts. The three classes of compounds known as *acids*, *bases*, and *salts* include the great majority of the compounds with which we shall be concerned. A few representatives of each class will be described in this chapter, so that their characteristic properties and reactions may be made clear.

The familiar acids. The liquids called acids, used so largely in the industries and in chemical laboratories, are all solutions of definite compounds in water. *Hydrochloric acid* is a solution of a gas called hydrogen chloride, which has the composition expressed in the formula HCl. *Nitric acid* is a solution of the liquid known as hydrogen nitrate, the formula of which is HNO_3. *Sulfuric acid* is a solution of the thick oily liquid called hydrogen sulfate, whose formula is H_2SO_4. For most purposes it is not necessary to make a distinction between the name of the compound and its solution in water, and both are frequently called acids.

Characteristics of acids. (1) All compounds forming acids in solution contain hydrogen. (2) The solutions have a sour taste. (3) They change the color of certain substances called *indicators*. Thus blue *litmus* (a dyestuff obtained from certain lichens) is turned red, as are the blue colors of most flowers, such as violets and corn flowers. (4) When brought in contact with certain metals, acids evolve hydrogen, and the metal dissolves. With hydrochloric acid and zinc the reaction is represented by the equation

$$2\ HCl + Zn \longrightarrow ZnCl_2 + H_2$$

Ionization of acids. When dissolved in water, the compounds forming acids all ionize into two kinds of ions. Of these hydrogen is always the cation (+), while the remainder of the molecule is the anion (−), thus:

$$HCl \longrightarrow H^+ + Cl^-$$

Since all acids produce hydrogen cations, while the anions of each are different, the properties which all acids have in common when in solution, for example, taste, and action on indicators and metals, must be attributed to the hydrogen ions. *We may therefore define an acid as a substance which produces hydrogen ions when dissolved in water.*

Undissociated acids. When compounds that form acids are perfectly free from water, or are dissolved in liquids, like benzene, which do not have the power of dissociating them into ions, they have no real acid properties. Under these circumstances they do not affect the color of indicators or have any of the properties characteristic of acids.

The familiar bases. The bases most used in the laboratory are *sodium hydroxide* ($NaOH$), *potassium hydroxide* (KOH), and *calcium hydroxide* ($Ca(OH)_2$). These are white solids, soluble in water — the latter sparingly so. The very soluble bases with most pronounced basic properties (including the three just mentioned) are sometimes called the *alkalies.*

Characteristics of bases. (1) All compounds forming bases in solution contain hydrogen and oxygen. (2) The solution of a base has a soapy feel and a bitter taste. (3) A base reverses the color change produced in indicators by acids, turning red litmus blue.

Ionization of bases. When dissolved in water, the molecules of the base dissociate into two kinds of ions. One of these is always composed of the group OH and is the anion. It is called the *hydroxyl ion.* The remainder of the molecule, which usually consists of a single atom, is the cation, thus:

$$NaOH \longrightarrow Na^+, OH^-$$

Since all bases produce hydroxyl anions, while the cations of each are different, the properties which all bases have in common when in solution must be due to the hydroxyl ions. *We may therefore define a base as a substance which produces hydroxyl ions when dissolved in water.*

Neutralization. When an acid and a base are brought together in solution in proper proportion, the characteristic properties of each disappear. As a rule the solution tastes neither sour nor bitter, but salty; it has no effect upon indicators. There can therefore be neither hydrogen ions nor hydroxyl ions in the solution. This action of an acid on a base is called *neutralization.*

A study of reactions of this kind has shown that hydrogen ions and hydroxyl ions cannot exist together in solution to any appreciable extent, but at once combine to form water. The following equations express the neutralization of three acids by three bases, water being formed in each case:

$$Na^+, OH^- + H^+, Cl^- \longrightarrow Na^+, Cl^- + H_2O$$
$$K^+, OH^- + H^+, NO_3^- \longrightarrow K^+, NO_3^- + H_2O$$
$$Ca^{++}, (OH^-)_2 + (H^+)_2, SO_4^{--} \longrightarrow Ca^{++}, SO_4^{--} + 2\,H_2O$$

Neutralization consists in the union of the hydrogen ion of an acid with the hydroxyl ion of a base, to form water.

Salts. It will be noticed that in neutralization the anion of the acid and the cation of the base are not changed, but remain as ions in the solution. If, however, the water is expelled by evaporation, these two ions slowly unite, and when the water becomes saturated with the substance so produced, it begins to separate in the form of a solid called a *salt*. *A salt, therefore, is a substance formed by the union of the anion of an acid with the cation of a base.*

A salt may also be obtained by the action of a metal on an acid:

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

and we may say that a salt is a compound obtained by displacing the hydrogen of an acid by a metal. The salt derived in this way from any given acid is said to be a salt of that acid. Thus, $ZnSO_4$ is a salt of sulfuric acid.

Characteristics of salts. (1) From the definition of a salt it will be seen that there is no element or group of elements which characterize salts. (2) Salts as a class have no peculiar taste. (3) With a few exceptions (to be explained later) they are without action on indicators. (4) When dissolved in water they form two kinds of ions.

Illustration of neutralization. Sometimes a soil becomes sour, or acid, owing to the formation of acids which are often derived from decomposing vegetable matter. Certain plants, such as mosses and huckleberries, will thrive in acid soil, but grass, clover, and grain crops will not. In such cases the soil must be *sweetened* by spreading calcium hydroxide (slaked lime) upon it to neutralize the acids present, the process being called *liming* the soil. An acid soil may be detected by moistening strips of blue litmus and covering them for a few minutes with the moist soil. Acids will turn the blue litmus bright red.

Extent of ionization. The question will naturally arise, When an acid, base, or salt dissolves in water, do all the molecules ionize, or only some of them? The experiments by which this question is answered cannot be described here. It has been found, however, that only a fraction of the molecules ionize. The percentage which ionizes in a given case depends upon several conditions, the chief of which are as follows:

1. ***The concentration of the solution.*** In concentrated solutions only a very small percentage of the molecules ionize. As the solution is diluted the percentage increases, and in dilute solutions it may be very large, though it is never complete in any ordinary solution.

2. ***The nature of the dissolved compound.*** At equal concentrations substances differ much among themselves in percentage of ionization. Most salts are about equally ionized. Acids and bases, on the contrary, show great differences. Some are freely ionized, while others are ionized to but a slight extent.

Strength of acids and bases. Since acid and basic properties are due to hydrogen ions and hydroxyl ions, the acid or base which will produce the greatest percentage of these ions at a given concentration must be regarded as the strongest representative of its class. The acids and bases described in the foregoing paragraphs are all quite strong. In 10 per cent solutions about half of the molecules are dissociated into ions, and this is also approximately the extent to which most salts are ionized at this same concentration.

Methods of expressing reactions between compounds in solution. Chemical equations representing reactions between substances in solution may represent the details of the reaction, or they may simply indicate the final products formed. Thus, if we wish to call attention to the details of the reaction between sodium hydroxide and hydrochloric acid in solution, representing the ions which take part in the reaction, we may write the equation as follows:

$$Na^+, OH^- + H^+, Cl^- \longrightarrow Na^+, Cl^- + H_2O$$

If we wish simply to represent substances taking part in the reaction and the final products formed, we write the equation thus:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Radicals. It has been emphasized that the hydroxyl group OH always forms the anion of a base. Similarly, the group NO_3 forms the anion of nitric acid; the group SO_4, the anion of sulfuric acid. *A group of elements which act together as a unit in chemical action is called a radical.*

Some of these radicals have been given special names. Thus, we have the hydroxyl radical OH, the nitrate radical NO_8, and the sulfate radical SO_4.

Displacement series. Upon bringing a piece of zinc into a solution of an acid, zinc passes into solution and hydrogen is evolved:

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$

In like manner, when zinc is placed in a solution of a salt of copper, such as the sulfate $CuSO_4$, zinc passes into solution, and a corresponding quantity of copper is precipitated:

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

On the other hand, copper has no effect upon a solution of zinc sulfate.

It has been found to be possible to arrange hydrogen and the metals in a table in such a way that any element in the list will displace any one below it from its salts and will in turn be displaced from its salts by any one above it. This list is called the *displacement series.*

DISPLACEMENT SERIES

1. Potassium
2. Sodium
3. Magnesium
4. Aluminium
5. Zinc
6. Iron
7. Tin
8. Lead
9. Hydrogen
10. Copper
11. Antimony
12. Bismuth
13. Mercury
14. Silver
15. Platinum
16. Gold

This table enables us to foretell many reactions. For example, from the positions of the two metals we should expect magnesium to displace tin from its salts:

$$Mg + SnCl_2 \longrightarrow MgCl_2 + Sn$$

We should not, however, expect iron to displace aluminium.

It is of especial interest to notice the position of hydrogen in the series. All the metals above it will evolve hydrogen from solutions of its salts (acids), while those below it will not. In the latter case, if any action takes place it must be preceded by oxidation.

Names of acids, bases, and salts. Since acids, bases, and salts are so intimately related to one another, it is very advantageous to give names to the three classes in accordance with some fixed system. The system universally adopted is as follows:

Naming of bases. All bases are called *hydroxides*. They are distinguished from each other by prefixing the name of the element which is in combination with the hydroxyl group. Examples: sodium hydroxide ($NaOH$); calcium hydroxide ($Ca(OH)_2$); copper hydroxide ($Cu(OH)_2$).

Naming of acids. The method of naming acids depends upon whether the acid consists of two elements or of three.

1. ***Binary acids.*** Acids containing only one element in addition to hydrogen are called *binary acids*. They are given names consisting of the prefix *hydro-*, the name of the second element present, and the termination *-ic*. Examples: hydrochloric acid (HCl); hydrosulfuric acid (H_2S).

2. ***Ternary acids.*** In addition to the two elements present in binary acids, most acids also contain oxygen. These acids therefore consist of three elements and are called *ternary acids*. It usually happens that the same three elements can unite in different proportions to make

several different acids. The most familiar one of these is given a name ending in the suffix *-ic*, while the one with less oxygen is given a similar name, but ending in the suffix *-ous*. Examples: nitric acid (HNO_3); nitrous acid (HNO_2).

Naming of salts. A salt derived from a binary acid is given a name consisting of the names of the two elements composing it, with the termination *-ide*. Example: sodium chloride ($NaCl$). All other binary compounds are named in the same way.

A salt of a ternary acid is named in accordance with the acid from which it is derived. A ternary acid with the termination *-ic* gives a salt with the name ending in *-ate*, while an acid with the termination *-ous* gives a salt with the name ending in *-ite*. The following table will make the application of these principles clear:

ACID	FORMULA	SALT	FORMULA
Hydrochloric	HCl	Sodium chloride	$NaCl$
Chlorous	$HClO_2$	Sodium chlorite	$NaClO_2$
Chloric	$HClO_3$	Sodium chlorate	$NaClO_3$

EXERCISES

1. Name three edible substances that taste sour. How could you prove the sour taste to be due to acids?

2. If your clothing should become spotted with acids in the laboratory, how would you try to remove the spots?

3. Compose a definition of a base, different from the one given in the text; of an acid; of a salt.

4. What weight of sodium hydroxide will be neutralized by 50 g. of hydrochloric acid? *Ans.* 54.85 g.

5. What weight of sulfuric acid will be neutralized by 40 g. of sodium hydroxide? *Ans.* 49.03 g.

6. Which will neutralize the most hydrochloric acid, 50 g. of sodium hydroxide or 50 g. of calcium hydroxide?

7. What weight of copper will be precipitated from a solution of copper sulfate by 60 g. of zinc? *Ans.* 58.34 g.

8. The most common of the ternary acids of sulfur has the formula H_2SO_4. What is its name? To what class (acids, bases, salts) do each of the following compounds belong: H_2SO_3, Na_2SO_4, Na_2SO_3, $Zn(OH)_2$, $Al(OH)_3$? Give the name of each.

9. Account for the fact that calcium hydroxide, *when perfectly dry*, has no action on litmus paper.

TOPIC FOR THEMES

The liming of soils. (Write to the director of your experiment station for bulletins.)

CHAPTER XIV

VALENCE

Definition of valence. A comparison of the composition of the compounds of hydrogen with the other elements brings to light an interesting fact illustrated in the formulas

HCl	H_2O	H_3N	H_4C
(hydrogen chloride)	(water)	(ammonia)	(marsh gas)

It will be seen that the various kinds of atoms differ in the number of hydrogen atoms that they are able to hold in combination. An atom of chlorine combines with but one hydrogen atom, an atom of oxygen with two, one of nitrogen with three, and one of carbon with four. It is convenient to have a name to designate that property of an element that determines the number of hydrogen atoms that its atom can hold in combination. It is called the *valence* of an element.

Classifications of elements according to their valences. Valence is merely the ratio between the numbers of two kinds of atoms which combine, and gives no information in regard to the intensity of affinity between the atoms. To express the valence of an element, we must select some standard for comparison, just as we do in the case of any other numerical quantity. Since one atom of hydrogen never combines with more than one atom of any other element, hydrogen is selected as the standard and is said to be *univalent.* Other elements, such as chlorine, iodine, and sodium, which combine with hydrogen atom for atom (HCl), are likewise said to be univalent. On the other hand, elements such as oxygen, sulfur, and calcium, one atom of which combines with two atoms of hydrogen or of other univalent elements, are said to be *bivalent*. Similarly, we have *trivalent* elements, such as nitrogen, and *quadrivalent* ones, such as carbon. No element is known whose valence exceeds 8, and with the majority of elements it does not exceed 4.

How the valence of an element may be inferred. The valence of an element may readily be inferred from the formula of the compound which it forms with hydrogen or other elements whose valence is known. The same method applies to radicals, for these are groups of atoms which act as a unit and on this account may be assigned valences just as though they were elements. Thus the radical OH must be univalent, since it combines with one atom of the univalent element sodium, as shown by the formula NaOH; the radical SO_4 must be bivalent, since it combines with two atoms of hydrogen, as shown by the formula H_2SO_4.

Valence and combination ratios. Elements or radicals having the same valence combine with each other atom for atom. When two elements having different valences combine, the combination will take place between such numbers of atoms as have equal valences. Thus *one* atom of a bivalent element or radical, such as zinc, has the same number of valences as *two* atoms of a univalent element, such as chlorine, namely two. Accordingly when such elements unite, the union will be between one atom of the bivalent element and two of the univalent element, as shown by the formula $ZnCl_2$. When a trivalent element unites with a bivalent element or radical, the union will be between two atoms of the trivalent element (total valence of 6) and three atoms of the bivalent (total valence of 6), as expressed in such formulas as Al_2O_3 and $Al_2(SO_4)_3$.

It is evident therefore that, knowing the valences of two elements or radicals, we can tell the probable formula of the compound which will be formed by their union; conversely, knowing the formula of the compound and the valence of one of the elements present, the valence of the other may be inferred. For example, if we know that iron is trivalent in the compound Fe_2S_3, then the sulfur must be bivalent; for the three atoms of sulfur will have the same total valence as the two atoms of iron, namely, 6. One atom of sulfur therefore has a valence of 2. In the case of a few compounds, such as hydrogen peroxide (H_2O_2), this principle does not hold good, but the discussion of these is beyond the scope of an elementary text.

Variable valence. Since many of the elements unite with each other in more than one ratio, it follows that some of the elements may have more than one valence. Thus, in the compound CO carbon has a valence of 2, while in the compound CO_2 it has a valence of 4. Similarly, in the oxides FeO and Fe_2O_3 iron has a valence of 2 and 3 respectively. It is the custom, therefore, to speak of the valence of an element in a given compound, or toward some given element.

Valence and the replacing power of atoms. Just as elements having the same valence combine with each other atom for atom, so, if they replace each other in a chemical reaction, they will do so in the same ratio. Thus, one atom of bivalent zinc displaces two atoms of univalent hydrogen, as is shown in the following equations:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
$$Zn(OH)_2 + H_2SO_4 \longrightarrow ZnSO_4 + 2\,H_2O$$

Similarly, one atom of bivalent calcium displaces one atom of bivalent zinc:

$$CaCl_2 + ZnSO_4 \longrightarrow CaSO_4 + ZnCl_2$$

Since many reactions, like those above, consist in an interchange of two elements, it is evident that a knowledge of the valence of the elements will assist us in writing the equations for the reactions.

Valence and charges on ions. We have represented ions as formed by the dissociation of molecules and as carrying electrical charges, thus:

$$HCl \longrightarrow H^{+} + Cl^{-}$$

Since hydrogen and chlorine are univalent, it will be seen that their valence is the same as the number of electrical charges they carry as ions. Similarly, calcium sulfate ionizes as follows:

$$CaSO_4 \longrightarrow Ca^{++} + SO_4^{--}$$

In this case both the calcium ion and the sulfate ion carry two electrical charges, and each is bivalent.

Table of valences. It will be convenient for reference to tabulate the valences of the most familiar elements and radicals. In the table which follows, some elements will be found in several different columns, since they have more than one valence. The table also indicates the number of electrical charges carried when the element or radical acts as an ion.

TABLE OF VALENCES

Valence	Positive Ions	Negative Ions	Not Ions
1	H, Na, K, Ag, NH_4	Cl, Br, I, OH, NO_3	
2	Ca, Ba, Mg, Zn, Hg, Cu, Fe, Sn	S, SO_4, CO_3	O
3	Al, Bi, Sb, Fe	PO_4	N, P
4	Sn	SiO_4	C, Si, S
5			N, P, As, Sb
6			S

EXERCISES

1. Write the formulas of the compounds that sodium (univalent) forms with each of the following elements or radicals: Cl(univalent); S(bivalent); SO_4(bivalent); PO_4(trivalent).

2. In the compounds whose formulas follow, the valence of one of the elements is indicated by a figure placed over the symbol. What is the valence of each of the other elements or radicals present in the compounds?

$$\overset{2}{Mg}Br_2;\ \overset{2}{Ca}O;\ \overset{2}{Ca}(OH)_2;\ \overset{2}{Ba}_3(PO_4)_2;\ \overset{1}{K}NO_3;\ \overset{1}{H}_3P$$

Verify your results by reference to the table.

3. Complete the following equations, supposing that the sodium or the calcium in the first compound changes places with the hydrogen of the second:

$$NaOH + HCl \longrightarrow \underline{\qquad} + \underline{\qquad}$$
$$2NaOH + H_2SO_4 \longrightarrow \underline{\qquad} + \underline{\qquad}$$
$$NaOH + H_3PO_4 \longrightarrow \underline{\qquad} + \underline{\qquad}$$
$$Ca(OH)_2 + HCl \longrightarrow \underline{\qquad} + \underline{\qquad}$$
$$Ca(OH)_2 + H_2SO_4 \longrightarrow \underline{\qquad} + \underline{\qquad}$$
$$Ca(OH)_2 + H_3PO_4 \longrightarrow \underline{\qquad} + \underline{\qquad}$$

CHAPTER XV

COMPOUNDS OF NITROGEN

Occurrence. The large quantity of nitrogen occurring in the atmosphere (p. 80) is practically all in the free state. In the materials composing the earth's crust, on the other hand, there occur in certain localities considerable deposits of nitrogen compounds, especially of sodium nitrate ($NaNO_3$). The latter compound is found in large quantities in Chile, and serves as the material from which many of the other compounds of nitrogen are prepared. Small quantities of nitrogenous compounds also occur in all productive soils. From these soils the nitrogen is taken up by plants and built into complex compounds known as *protein* matter. Animals feeding on these plants assimilate the nitrogenous matter, which becomes an essential part of the animal tissue (p. 83).

While a great many compounds of nitrogen are known, it is desirable at this time to discuss only a few of the simpler ones.

AMMONIA (NH_3)

Several compounds consisting exclusively of nitrogen and hydrogen are known, but only one, ammonia, need be considered here.

Preparation of ammonia. Ammonia is prepared in the laboratory by a different method from the one which is used commercially.

1. ***Laboratory method.*** In the laboratory, ammonia is prepared from ammonium chloride (NH_4Cl), a white solid obtained in the manufacture of coal gas (p. 210). In this compound the group NH_4 acts as a univalent radical and is known as *ammonium*. When ammonium chloride is warmed with sodium hydroxide, the ammonium radical and sodium change places, the reaction being expressed in the following equation:

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH$$

The ammonium hydroxide (NH_4OH) so formed is unstable and breaks down into water and ammonia:

$$NH_4OH \longrightarrow NH_3 + H_2O$$

Calcium hydroxide ($Ca(OH)_2$) is frequently used in place of the more expensive sodium hydroxide, the equations being

$$2\,NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\,NH_4OH$$
$$2\,NH_4OH \longrightarrow 2\,H_2O + 2\,NH_3$$

The ammonium chloride and calcium hydroxide are mixed together and placed in a flask *A*, arranged as shown in Fig. 55. The mixture is gently warmed, when ammonia is evolved as a gas and, being much lighter than air, is collected in *B* by displacement of air, as shown in the diagram.

2. ***Commercial method.*** Most of the ammonia of commerce is obtained by heating soft coal in the absence of air, as is done in the manufacture of illuminating gas or coke (p. 210). Among the by-products of this operation is an impure solution of ammonia in water, known as *gas liquor.* This is treated with lime and heated, the ammonia being driven out as a gas. The gas may be dissolved again in pure, cold water, forming *aqua ammonia,* or the ammonia water of commerce.

Preparation from hydrogen and nitrogen. When electric sparks are passed for some time through a mixture of hydrogen and nitrogen, a small percentage of the two elements in the mixture is changed into ammonia. The yield of ammonia is very small, for the reason that the compound is decomposed by the spark, and a point is soon reached when the speed of its decomposition is as great as the speed of its formation. These facts are expressed in the equation

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$$

This recalls the similar relation between oxygen and ozone.

The Haber process. When a mixture of nitrogen and hydrogen subjected to a pressure of 200 atmospheres is heated to about 500° in contact with finely divided iron, a larger percentage of ammonia is formed. This is dissolved in water as fast as formed, and the remaining gases are again conducted over the iron. The process thus becomes continuous, more nitrogen and hydrogen being introduced as needed. Large factories are being built in Germany for making ammonia by this process for use in fertilizers. The nitrogen used is obtained from the air, and the hydrogen from water.

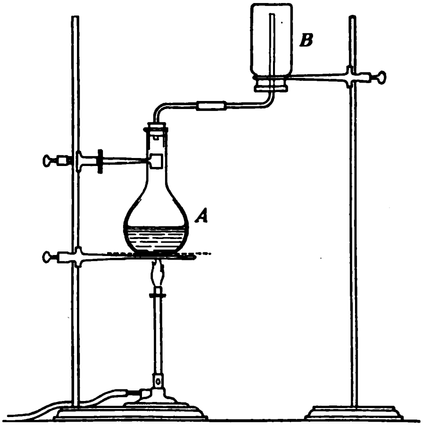


FIG. 55. The preparation of ammonia in the laboratory

Properties. Under ordinary conditions ammonia is a gas which is little more than half as heavy as air. It is easily condensed into a colorless liquid, and can now be purchased in this form. The gas is colorless and has a strong, suffocating odor often noticed about decaying organic matter.

It is extremely soluble in water, 1 liter of water at 0° and 760 mm. pressure dissolving 1298 liters of the gas, and at 20°, 710 liters. In dissolving such large volumes of the gas the water expands considerably, so that the density of the solution is less than that of water, the most concentrated commercial solutions having a density of 0.88.

Chemical conduct. Ammonia will not support combustion, nor will it burn under ordinary conditions. In an atmosphere of oxygen it burns with a feeble, yellowish flame. When quite dry, it is not a very active substance, but when moist, it combines with a great many substances, particularly with acids.

Uses. It has been stated that ammonia can be condensed to a liquid by the application of pressure. If the pressure is removed from the liquid so obtained, this liquid rapidly passes again into the gaseous state, and in so doing absorbs a great deal of heat. Advantage is taken of this fact in the manufacture of ice. Large quantities of ammonia are also used in the manufacture of ammonium compounds.

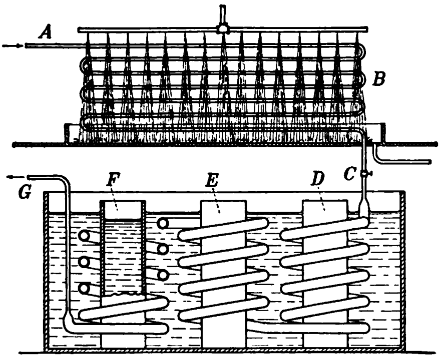


Fig. 56. Diagram of an ammonia ice machine

The manufacture of ice. Fig. 56 illustrates the method of manufacturing ice. The ammonia gas is liquefied in the pipes *A*, *B* by means of a compression pump. The heat generated by liquefaction is absorbed by water flowing over the pipes. The pipes lead into a large brine tank, a cross section of which is shown in the figure. Into the brine (concentrated solution of calcium chloride) contained in this tank are dipped the vessels *D*, *E*, *F*, filled with pure water. The pressure is removed from the liquid ammonia as it passes through the expansion valve *C* into the pipes immersed in the brine, and the heat absorbed by the rapid evaporation of the liquid lowers the temperature of the brine below zero. The water in *D*, *E*, *F* is thereby frozen into cakes of ice. The gaseous ammonia resulting from the evaporation of the liquid escapes at *G* and is again liquefied, and the process is repeated.

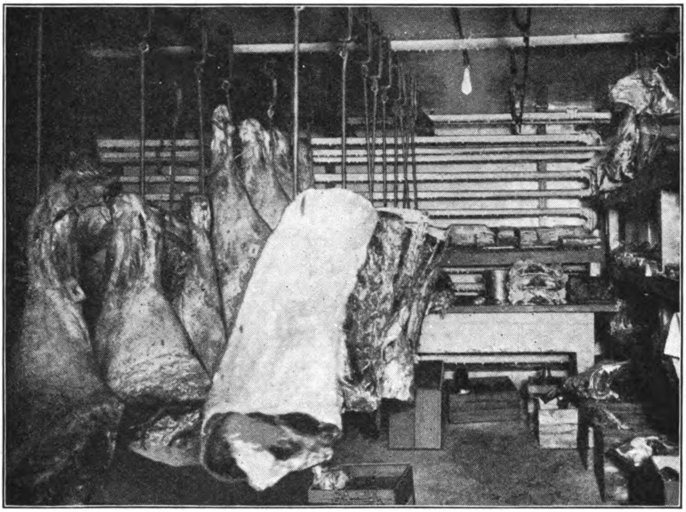


FIG. 57. The interior of a cold-storage room

Cold storage. The temperature of a room may be kept very low by surrounding it with pipes into which liquid ammonia is forced and allowed to vaporize. The vapor is conducted away and again compressed to the liquid state and again returned, so that the process becomes continuous. The cold-storage plants now so largely used for preventing the decay of food products are constructed on this principle. Fig. 57 shows a corner of a cold-storage room. The pipes containing the ammonia soon become covered with frozen moisture.

Ammonium hydroxide (NH_4OH). The solution of ammonia in water, commonly called *aqua ammonia*, has strong basic properties. It turns red litmus blue; it has a soapy feel; it neutralizes acids, forming salts with them. It seems certain, therefore, that when ammonia dissolves in water it combines chemically with it according to the equation

$$NH_3 + H_2O \longrightarrow NH_4OH$$

and that it is the substance NH_4OH, called ammonium hydroxide, which has the basic properties, dissociating into the ions NH_4 and OH. The separation of the pure hydroxide from its solutions has not been accomplished, for as the solution becomes concentrated, the compound decomposes again into ammonia and water:

$$NH_4OH \longrightarrow NH_3 + H_2O$$

The solution of ammonia in water, therefore, constitutes a state of equilibrium between ammonia and water, on the one hand, and ammonium hydroxide, on the other. This condition is conveniently expressed in the following way:

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

Aqua ammonia is a good solvent for grease and is a familiar household article.

The ammonium radical. The univalent radical NH_4 plays the part of a metal in many chemical reactions, and is called *ammonium*. The ending *-ium* is given to the name to indicate the metallic properties of the substance, since the names of the metals in general have that ending. The salts formed by the action of the base ammonium hydroxide on acids are called *ammonium salts.* Thus, with hydrochloric acid, ammonium chloride (NH_4Cl) is formed, in accordance with the equation

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

Combination of nitrogen with hydrogen by volume. Ammonia can be decomposed into nitrogen and hydrogen by passing electric sparks through the gas. Accurate measurement has shown that *2 volumes of ammonia yield 1 volume of nitrogen and 3 volumes of hydrogen.* These relations may be represented graphically as follows:

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

ACIDS OF NITROGEN

The most important of the acids of nitrogen are the following: nitric acid (HNO_3) and nitrous acid (HNO_2).

Nitric acid (HNO_3). This acid is prepared from sodium nitrate ($NaNO_3$), which occurs in nature in large quantities.

Preparation of nitric acid. When sodium nitrate is treated with concentrated, cold sulfuric acid, no chemical action seems to take place. If, however, the mixture is heated in a retort *A*, nitric acid is given off as a vapor and may be easily condensed to a liquid by passing the vapor into a tube *B* surrounded by cold water, as shown in Fig. 58.

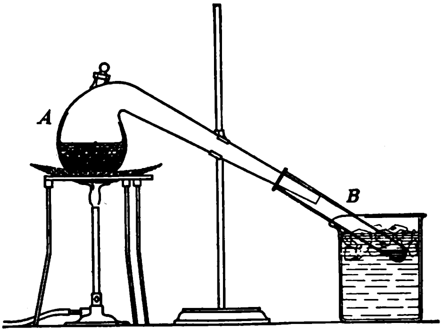


FIG. 58. The preparation of nitric acid in the laboratory

An examination of the liquid left in the retort shows that it contains sodium acid sulfate ($NaHSO_4$), only half of the hydrogen of sulfuric acid having been replaced by sodium. The reaction may be represented by the equation

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

The commercial preparation of nitric acid. Fig. 59 illustrates a form of apparatus used in the preparation of nitric acid on a large scale. Sodium nitrate and sulfuric acid are heated in the iron retort *A*. The resulting acid vapors pass in the direction indicated by the arrows, and are condensed in the glass tubes *B*, which are covered with cloth kept cool by streams of water. These tubes are inclined so that the liquid resulting from the condensation of the vapors runs back into *C* and is drawn off into the large vessel *D*.

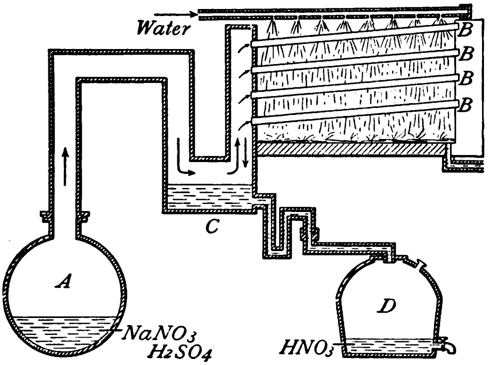


FIG. 59. The commercial preparation of nitric acid

Preparation of nitric acid from air. When electric discharge takes place through a mixture of oxygen and nitrogen (air), a small percentage of oxides of nitrogen is formed. This can be increased by having the mixture pass through an electric arc which has been drawn out to a great size by magnets (Fig. 60). The oxides so obtained combine with water to form dilute nitric acid. This method for preparing nitric acid (known as the Birkeland and Eyde process) has come into extensive use in recent years in Norway, since the necessary electrical energy is generated at a very low cost by the waterfalls abounding in that country. The dilute nitric acid obtained is neutralized with lime (CaO) and the resulting calcium nitrate sold for use as a fertilizer under the name *air saltpeter.*

Properties of nitric acid. Pure nitric acid (hydrogen nitrate) is a colorless liquid which boils at about 86° and has a density of 1.56. The concentrated acid of commerce contains about 68 per cent of the acid, the remainder being water. Such a mixture has a density of 1.4. The concentrated acid fumes somewhat in moist air, and has a sharp, choking odor.

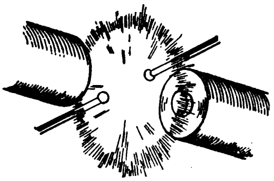


FIG. 60. Form of the electric arc employed in the Birkeland and Eyde process

Chemical conduct. The most important chemical reactions of nitric acid are the following:

1. ***Acid action.*** Nitric acid has all the characteristics of a *strong* acid. It changes blue litmus red, and has a sour taste in dilute solutions. It gives hydrogen ions in solution, and neutralizes bases, forming salts. It also acts upon the oxides of most metals, forming a salt and water, thus:

$$CuO + 2\,HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

2. ***Decomposition on heating.*** When nitric acid is boiled or when it is exposed for some time to sunlight, it suffers a partial decomposition according to the equation

$$4\,HNO_3 \longrightarrow 2\,H_2O + 4\,NO_2 + O_2$$

The substance NO_2 (called nitrogen dioxide) is a brownish gas which is readily soluble in water and in nitric acid. It therefore dissolves in the undecomposed acid, and imparts to it a yellowish or reddish color. Concentrated nitric acid highly charged with this substance is called *fuming nitric acid.*

3. ***Oxidizing action.*** Because of its easy decomposition, nitric acid is a good oxidizing agent. Under ordinary circumstances, when acting as an oxidizing agent, it is decomposed according to the equation

$$2\,HNO_3 \longrightarrow H_2O + 2\,NO + 3[O]$$

The oxygen is taken up by the substance oxidized and is not set free, which fact is indicated in the equation by placing the symbol for oxygen in brackets. Thus, if carbon is oxidized by nitric acid, the oxygen combines with carbon, forming carbon dioxide (CO_2):

$$C + 2\,[O] \longrightarrow CO_2$$

4. ***Action on metals.*** Nitric acid acts in two different ways upon metals: (1) With *dilute* nitric acid the metals *above* hydrogen in the displacement series (p. 112), such as zinc, evolve hydrogen:

$$Zn + 2\,HNO_3 \longrightarrow Zn(NO_3)_2 + H_2$$

(2) With *concentrated* nitric acid none of the metals evolve hydrogen, but oxidation takes place forming a nitrate together with a gas called nitric oxide (NO). With copper the reaction is expressed in the equation

$$3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$$

A similar action often occurs when dilute nitric acid acts upon metals below hydrogen in the displacement series.

Uses. Nitric acid has countless uses in the industries and in chemical laboratories. It is most extensively used in the manufacture of explosives of various kinds and of celluloid and artificial dyes.

Salts of nitric acid; nitrates. The salts of nitric acid are called *nitrates.* Many of these salts will be described in the study of the metals. They are all soluble in water, and when heated to a high temperature, undergo decomposition. In a few cases a nitrate, on being heated, evolves oxygen, forming a *nitrite*:

$$2\,NaNO_3 \longrightarrow 2\,NaNO_2 + O_2$$

In other cases the decomposition goes farther, and the metal is left as oxide:

$$2\,Pb(NO_3)_2 \longrightarrow 2\,PbO + 4\,NO_2 + O_2$$

The nitrates are especially used in the manufacture of gunpowder, sulfuric acid, nitric acid, and as a fertilizer.

Nitrous acid (HNO_2). It is an easy matter to obtain sodium nitrite ($NaNO_2$) by heating sodium nitrate, as explained in the previous paragraph. Now when sodium nitrite is treated with an acid, such as sulfuric acid, it is decomposed and nitrous acid is set free:

$$NaNO_2 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_2$$

The acid is very unstable, however, and decomposes into water and oxides of nitrogen. Sodium nitrite is used in the manufacture of artificial dyes.

OXIDES OF NITROGEN

The most important of the oxides of nitrogen are the following:

Nitrous oxide (N_2O)	a colorless gas
Nitric oxide (NO)	a colorless gas
Nitrogen dioxide (NO_2)	a reddish-brown gas
Nitrogen trioxide (N_2O_3) . . .	known only at low temperatures
Nitrogen pentoxide (N_2O_5) . .	a white solid

Nitrous oxide (laughing gas) (N_2O). This gas is most readily prepared by heating ammonium nitrate:

$$NH_4NO_3 \longrightarrow 2\,H_2O + N_2O$$

It is colorless, is somewhat soluble in water, and in solution has a slightly sweetish taste. When inhaled, it produces a kind of hysteria (hence the name *laughing gas*) and, if taken in large amounts, insensibility to pain and unconsciousness. It was the first substance to be used as an anæsthetic in surgery, and is still used in minor operations, such as those of dentistry.

Nitrous oxide is a very energetic oxidizing agent. Substances such as carbon, sulfur, iron, and phosphorus burn in it almost as brilliantly as in oxygen, forming oxides and setting free nitrogen. Evidently the oxygen in nitrous oxide is not held in very firm combination by the nitrogen.

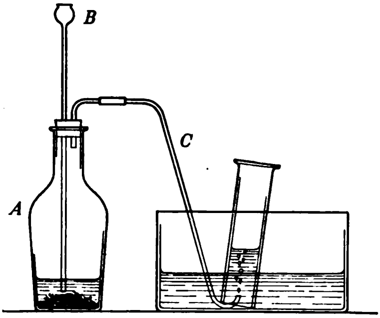


Fig. 61. The preparation of nitric oxide

Nitric oxide (NO). Nitric oxide is most conveniently prepared by the action of nitric acid upon copper:

$$3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$$

The metal is placed in the flask *A* (Fig. 61), and the acid added slowly through the funnel tube *B*. The gas escapes through *C* and is collected over water. Nitric oxide is a colorless gas slightly heavier than air. Unlike nitrous oxide, it does not part with its oxygen easily, and burning substances introduced into this gas are usually extinguished.

When nitric oxide comes into contact with oxygen or air, it at once combines with the oxygen, even at ordinary temperatures, forming a reddish-brown gas, NO_2, which is called *nitrogen dioxide*:

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

To show the formation of nitrogen dioxide from nitric oxide and oxygen, a tube is filled with the oxide, inverted in water, and pure oxygen is passed into it, as shown in Fig. 62. As each bubble of oxygen enters, it unites with the nitric oxide to form the reddish-brown dioxide. In a few minutes the color fades (because of the action of water upon the dioxide), and the water slowly rises in the tube.

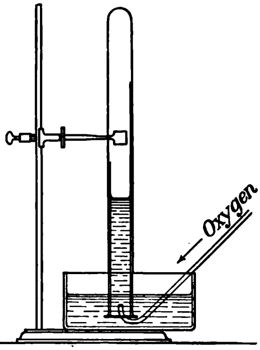


FIG. 62. The formation of nitrogen dioxide from nitric oxide and oxygen

Nitrogen dioxide (NO_2). This gas, as we have just seen, is formed by allowing nitric oxide to come into contact with oxygen. It can also be made by heating certain nitrates, such as lead nitrate (p. 131). It is a reddish-brown gas of unpleasant odor, and is poisonous when inhaled. It gives up a part of its oxygen to burning substances, acting as an oxidizing agent:

$$NO_2 \longrightarrow NO + [O]$$

Nitrogen tetroxide. At lower temperatures nitrogen dioxide becomes paler in color and condenses to a pale-yellow liquid. It has been shown that this paler gas has the formula N_2O_4, and it is called *nitrogen tetroxide*. At ordinary temperatures the gas is a mixture of the two, and we may express this relation thus:

$$\underset{\text{high temperatures}}{\text{Nitrogen dioxide, } 2\,NO_2} \rightleftarrows \underset{\text{low temperatures}}{\text{nitrogen tetroxide, } N_2O_4}$$

Acid anhydrides. The oxides N_2O_3 (nitrogen trioxide) and N_2O_5 (nitrogen pentoxide) are rarely prepared and need not be separately described. They bear a very interesting relation to the acids of nitrogen. When dissolved in water they combine with the water, forming acids:

$$N_2O_3 + H_2O \longrightarrow 2\,HNO_2$$
$$N_2O_5 + H_2O \longrightarrow 2\,HNO_3$$

Many other oxides act in the same way, combining with water to form an acid. Such oxides are called *acid anhydrides.*

EXERCISES

1. Perfectly dry ammonia does not affect litmus paper. Explain.

2. Can ammonia be dried by passing the gas through concentrated sulfuric acid? Explain.

3. Why is brine used in the manufacture of artificial ice?

4. Discuss the energy changes which take place in the manufacture of artificial ice.

5. Write the equations for the reactions taking place when ammonium hydroxide is neutralized by hydrochloric, sulfuric, and nitric acids respectively.

6. It is said that nitric acid is formed during thunderstorms. How would you account for its formation?

7. What does the word *ammonia* mean (consult dictionary)?

8. Why is nitric acid said to be a strong acid?

9. What are the properties of ammonia that make it suitable for use in the preparation of artificial ice?

10. How many liters of ammonia at 0° and 760 mm. pressure will 1 liter of water dissolve? *Ans.* 1298 liters. What would this volume of ammonia weigh? *Ans.* 1000.5 g. What weight of ammonium chloride would be necessary to prepare it? *Ans.* 3142.46 g.

TOPICS FOR THEMES

The manufacture of ice. (If possible, visit an ice plant.)

The manufacture of nitric acid from the air (Duncan, Chemistry of Commerce, chapter on Fixation of Nitrogen).

The use of nitrous oxide as an anæsthetic.

CHAPTER XVI

EQUILIBRIUM; MASS ACTION

Reversible reactions. We have met with a number of reactions which are especially interesting because they can go in either direction. Thus, when we heat mercuric oxide, we obtain mercury and oxygen; while if we heat mercury in contact with oxygen, we obtain mercuric oxide (p. 6). These facts are represented in the following way:

$$2\,HgO \rightleftarrows 2\,Hg + O_2$$

In a similar way we have found that when an electric discharge is passed through a mixture of nitrogen and hydrogen, we get a small quantity of ammonia (p. 123); yet when the discharge is passed through ammonia, we get hydrogen and nitrogen:

$$2\,NH_3 \rightleftarrows N_2 + 3\,H_2$$

Such reactions are known as *reversible reactions.*

Equilibrium. If we remember that the materials taking part in a reaction are made up of great numbers of molecules all of which are in rapid motion and are constantly changing their relations to each other, it is not difficult to see why some molecules should be decomposing while others are forming. In time, however, a condition will be reached in which the changes in the one direction will just offset those in the other. The *average* percentage of each material present will then remain unchanged. This condition of affairs is called *equilibrium.* Thus, ammonia, hydrogen, and nitrogen come to equilibrium in the presence of electric discharge when there is about 7 per cent of ammonia and 93 per cent of uncombined nitrogen and hydrogen.

Mass action. Suppose, when equilibrium has been reached, we add an additional quantity of one of the acting substances — say hydrogen in the case just mentioned. This will make it easier for the nitrogen to act upon the hydrogen, for the two kinds of molecules will now meet more frequently. It will not at all affect the rate at which ammonia is decomposing. The net effect will therefore be to bring about a new equilibrium in which a larger percentage of ammonia is present. The effect produced by an excess of one of the reacting materials is called *mass action.*

Changing an equilibrium to a completed reaction. If we were to withdraw the ammonia as fast as it is formed, before it has time to decompose, the reaction ought to go on until either the hydrogen or the nitrogen is used up. This is just what takes place if during the discharge the gases are inclosed over water containing acid, with which the ammonia combines.

The point of equilibrium can therefore be changed or the equilibrium converted into a completed reaction by changing the acting mass of the substances taking part in the reaction.

Equilibrium in solution. In aqueous solution the molecules of an electrolyte keep dissociating into ions, while the ions, on meeting, recombine to form molecules, the result being an equilibrium between the two conditions, thus:

$$HNO_3 \rightleftarrows H^+ + NO_3^-$$

If we mix two electrolytes, the equilibrium reached becomes much more complicated, for any positive ion may unite with any negative one. At equilibrium all possible ions and combinations of ions will be present. Thus, when we mix sodium nitrate and sulfuric acid in the preparation of nitric acid, we have present the ions Na^+, NO_3^-, H^+, and SO_4^{--}, together with the molecules $NaNO_3$, Na_2SO_4, $NaHSO_4$, HNO_3, and H_2SO_4.

Completion of reactions in solution. The chemist makes use of reactions to secure various compounds in pure condition, and he wishes the yield to be as large as possible. Reactions which stop short of completion and end in an equilibrium are not suited to manufacturing purposes, unless means can be found to break up the condition of equilibrium and bring the reaction to a definite conclusion. There are three conditions under which this may be accomplished.

1. ***A volatile gas may be formed.*** If the reaction is conducted under such conditions that one of the products is a gas *insoluble in the solvent*, the gas will make its escape as fast as it is formed, and this action will continue until one or the other of the ions taking part in its formation is used up.

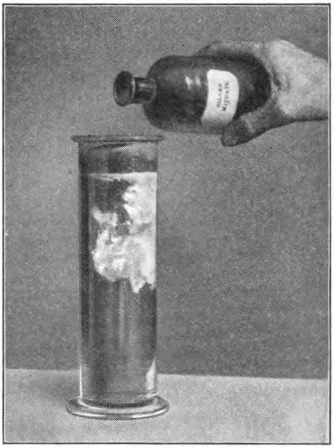


FIG. 63. Precipitation of silver chloride

Thus, when we mix sulfuric acid and sodium nitrate, no visible reaction takes place. But if we heat the mixture above the boiling point of nitric acid, all of this substance formed in the equilibrium between the H^+ and the NO_3^- ions is converted into a gas insoluble in sulfuric acid. The nitric acid distills away until the NO_3^- ions are used up. We then have a completed reaction expressed in the equation

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

It is in this way that most acids are prepared. Their salts are heated with some acid of high boiling point, usually with sulfuric acid, which boils at 338°.

2. ***An insoluble solid may be formed.*** When hydrochloric acid (HCl) and silver nitrate ($AgNO_3$) are brought together in solution, we have in addition to these two compounds the ions H^+, Cl^-, Ag^+, NO_3^-, and the new combinations HNO_3 and $AgCl$. One of these, namely, silver chloride ($AgCl$), is insoluble in water and as fast as formed separates from the solution as a curdy white *precipitate* (Fig. 63). The reaction therefore continues till either the Ag^+ or the NO_3^- is used up, the completed equation being

$$H^+ + Cl^- + Ag^+ + NO_3^- \longrightarrow H^+ + NO_3^- + AgCl$$

3. ***Two different ions may unite to form an undissociated molecule.*** When we bring together sodium hydroxide and hydrochloric acid in solution, we have the ions H^+, Cl^-, Na^+, and OH^-. The H^+ ions and the OH^- ions unite to form molecules of water *which do not again part into ions* save to a very slight extent. This leaves only the ions of $NaCl$ in solution, the equation being

$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow H_2O + Na^+ + Cl^-$$

Neutralization is practically a completed reaction *because water is so little ionized.*

Hydrolysis. While water is very little ionized, nevertheless it forms *some* ions. Moreover, when a salt is dissolved in water to form a dilute solution, the relative mass of the water is very great. The reaction of neutralization is therefore reversed to a *slight extent*, forming a small amount of free base and of free acid, thus:

$$NaNO_2 + H_2O \rightleftarrows NaOH + HNO_2$$

A reaction of this kind, in which water acts upon a salt to form a base and an acid, is called *hydrolysis.* If the base formed in hydrolysis is very weak and the acid is strong, the solution will turn blue litmus red, as is true with all salts of aluminium. If the base is very strong and the acid weak, the solution will turn red litmus blue, as is the case with many salts of sodium. If both the acid and the base are weak, then the compound may be *completely* hydrolyzed.

EXERCISES

1. Can you mention any reversible reactions, other than those given in this chapter?

2. Suggest a method for the preparation of hydrogen chloride.

3. Would silver nitrate produce a precipitate when added to a solution of sodium chloride (common salt)? If so, how would the precipitate compare in composition with that produced when silver nitrate is added to hydrochloric acid?

4. Barium sulfate ($BaSO_4$) is a white insoluble compound much used as a pigment in making paints. Suggest a method for preparing it.

5. Is the reaction $NH_3 + H_2O \longrightarrow NH_4OH$ reversible? If so, state the conditions under which it will go in each direction.

6. Is the reaction expressed by the equation $2\,H_2 + O_2 \longrightarrow 2\,H_2O$ reversible? If so, state the conditions under which it will go in each direction.

7. Carbonic acid is a very weak acid, while sodium hydroxide is a strong base. How will a solution of sodium carbonate act towards litmus paper?

CHAPTER XVII

SULFUR AND ITS COMPOUNDS

Occurrence. The element sulfur has been known from the earliest times. It is widely distributed in nature, and occurs in large quantities in the uncombined form, especially in the neighborhood of volcanoes. Sicily has long been famous for its sulfur mines, and in more recent years large deposits have been found in Louisiana. It is occasionally found in well-formed crystals.

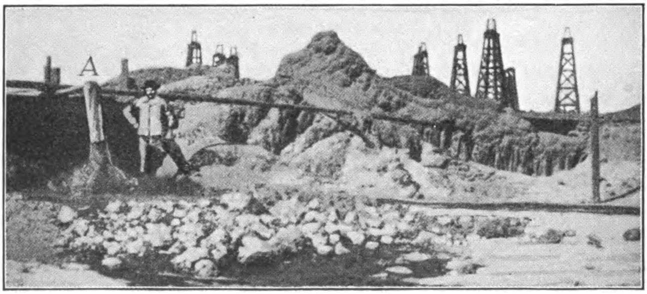


FIG. 64. The flow of liquid sulfur from a well (pipe *A*) in Louisiana

In combination, sulfur occurs abundantly in the form of sulfides and sulfates. In smaller amounts it is found in a great variety of minerals and is a constituent of many vegetable and animal substances, especially of the yolk of eggs.

Extraction of sulfur. In Louisiana the sulfur occurs in deposits far underground and covered with quicksand so that it cannot be mined. One of these deposits lies at a depth of 700 feet, is circular in shape, and is about half a mile in diameter and 500 feet in thickness. Wells are drilled into the deposit, and superheated water (above 160°) is forced down through suitable pipes. The hot water melts the sulfur, which is then forced up a separate pipe by compressed air (Fig. 64). The liquid sulfur then solidifies in very large blocks (Fig. 65). A single well has produced 500 tons daily, and the product is 99.5 per cent pure. About 250,000 tons are produced annually from this deposit.

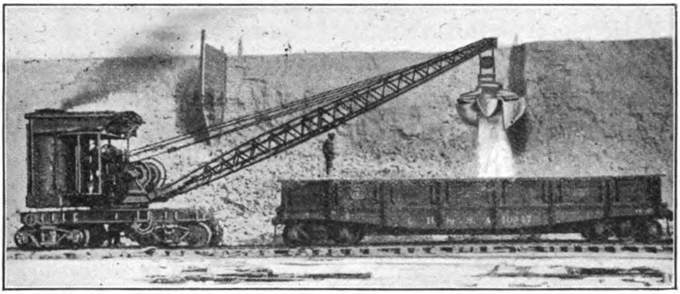


Fig. 65. Loading a block of sulfur on a car in Louisiana

In Sicily a very simple but wasteful method is used to separate sulfur from the rock and earthy materials with which it is mixed. The material is piled up in heaps and set on fire, and the heat from the burning of a part of the sulfur serves to melt another portion, which collects as a liquid at the bottom of the pile. This is drained off and purified by distillation in a retort-shaped vessel *A* (Fig. 66), the exit tube of which opens into a cooling chamber, *B*, of brickwork.

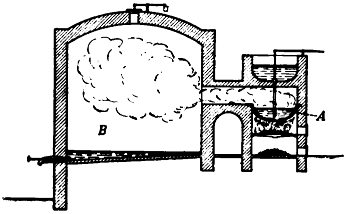


Fig. 66. A sulfur still

When the sulfur vapor first enters the cold chamber it condenses as a fine crystalline powder called *flowers of sulfur.* As the condensing chamber becomes warm, the sulfur condenses as a liquid and is drawn off into cylindrical molds, the product being called *roll sulfur* or *brimstone.*

Varieties of sulfur. Sulfur exists in a number of quite different forms. Several other elements occur in a number of different forms, but the forms of sulfur are unusually numerous and are easy to obtain. The best-known forms are the following:

1. ***Ordinary, or rhombic, sulfur.*** When sulfur crystallizes from solution in liquids (notably from carbon disulfide) it is obtained in compact yellow crystals which melt at 114.5° and have a density of 2.06. This is called *rhombic sulfur* (Fig. 67), and roll sulfur is composed largely of this variety.

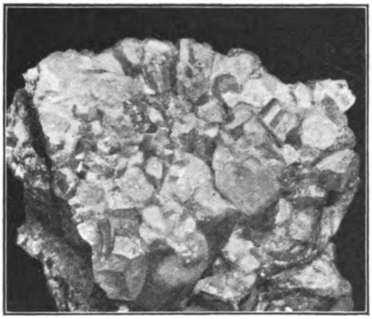


FIG. 67. Natural crystals of rhombic sulfur

2. ***Prismatic, or monoclinic, sulfur.*** When melted sulfur is allowed to cool until a part of the liquid has solidified, and the remaining liquid is then poured off, it is found that the solid sulfur remaining in the vessel is in the form of fine needle-shaped crystals, which melt at 119° and have a density of 1.96. The needle-shaped form is called *monoclinic sulfur.* At all temperatures below 96° the needle-shaped crystals break up more or less rapidly into little crystals of the rhombic variety.

3. ***Plastic sulfur.*** When boiling sulfur is poured into cold water it assumes a gummy, doughlike form, which is quite

elastic. This can be seen in a very striking manner by distilling sulfur from a small, short-necked retort (such as is represented in Fig. 68) and allowing the liquid to run directly into water. In a few days it becomes brittle and in part passes over into ordinary rhombic sulfur.

4. ***White, or amorphous, sulfur.*** If freshly prepared plastic sulfur is treated with carbon disulfide, the rhombic sulfur in it dissolves and a nearly colorless residue remains which is not crystalline. This is called *white*, or *amorphous, sulfur.* Ordinary flowers of sulfur consist of a mixture of rhombic crystals and amorphous particles.

Properties of ordinary sulfur. Sulfur is a pale-yellow crystalline solid, without marked taste and with but a faint odor. It is insoluble in water, but is freely soluble in a few liquids, notably in carbon disulfide. It melts at 114.5°. Just above the melting point it forms a rather thin, straw-colored liquid. As the temperature is raised, this liquid turns darker in color and becomes thicker, until at about 235° it is almost black and is so thick that the vessel containing it can be inverted without danger of the liquid running out. At higher temperatures it becomes thin once more, and boils at 444.6°, forming a yellowish vapor. When the vapor cools, the same changes take place in reverse order.

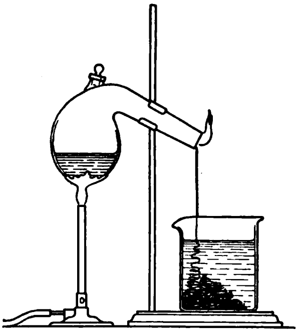


FIG. 68. The preparation of plastic sulfur

Chemical conduct of sulfur. Sulfur burns in oxygen or in the air with a pale-blue flame, forming sulfur dioxide (SO_2). Most metals when heated with sulfur combine directly with it, forming metallic sulfides. In some cases the action is so energetic that the mass becomes incandescent, as is the case with iron. This conduct recalls the action of oxygen upon metals, and in general the metals which combine readily with oxygen are apt to combine with sulfur.

Uses of sulfur. Large quantities of sulfur are used in the manufacture of gunpowder, vulcanized rubber, carbon disulfide, sulfur dioxide, sulfuric acid, and salts of various kinds. It is also used extensively in the manufacture of insecticides for use in orchards and vineyards.

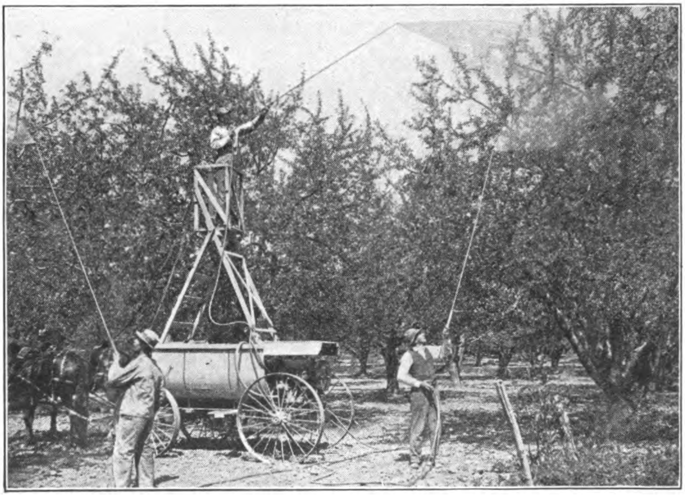


FIG. 69. Spraying an orchard of fruit trees with lime-sulfur spray

Lime-sulfur spray. The chief sulfur insecticide is known as *lime-sulfur spray.* It is made by boiling sulfur with slaked lime, by which process a deep-red liquor is obtained, consisting essentially of a solution of sulfides of calcium (CaS_4 and CaS_5). The liquid is a very efficient insecticide, particularly for scale, and it is also a fungicide. Large quantities of it are used for spraying fruit trees (Fig. 69).

Vulcanized rubber. Natural rubber (caoutchouc) is very soft and elastic, and becomes fluid at about 120°. To render it suitable for most purposes it must be *vulcanized.* This process consists in working into the caoutchouc about 2 to 3 per cent of sulfur, though for some purposes other materials, such as zinc oxide and antimony sulfide, are used. The sulfur is worked into the warm rubber or the rubber is immersed in liquids containing sulfur. Vulcanized rubber is more elastic than caoutchouc and much less sticky.

When a larger percentage of sulfur is added and the product is heated somewhat higher, a black, horny material is obtained called *hard rubber, vulcanite,* or *ebonite.* It is used for making such articles as combs, buttons, fountain pens, and electrical insulators.

The crude rubber is obtained from the milky sap of certain species of trees growing in tropical countries, particularly in Brazil. The sap is collected in buckets, and paddle-shaped sticks are dipped in and then dried over a fire. The process is repeated until a lump of crude rubber has been collected, and this is then loosened from the stick and sent to the market.

COMPOUNDS OF SULFUR WITH HYDROGEN

Hydrogen sulfide (H_2S). This gas is found in the vapors issuing from volcanoes, and in solution in many natural waters. It is formed when organic matter containing sulfur undergoes decay, just as, under similar circumstances, ammonia is formed from nitrogenous matter.

Preparation. Since hydrogen sulfide is a gas which is a little soluble in water, it can be prepared *by treating a sulfide with an acid* (p. 138). Iron sulfide (FeS) is usually employed:

$$FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S$$

A convenient apparatus is shown in Fig. 70. A few lumps of iron sulfide are placed in the bottle *A* and dilute acid is added a little at a time through the funnel tube *B*, the gas escaping through the tube *C*.

Properties. Hydrogen sulfide is a colorless gas having a weak, disagreeable taste and a most offensive odor suggesting rotten eggs. At ordinary temperatures it is but sparingly soluble in water; in boiling water it is not soluble at all. When inhaled in concentrated form it acts as a violent poison, and even when much diluted with air, produces headache, dizziness, and nausea. It is a little heavier than air, having a density of 1.18.

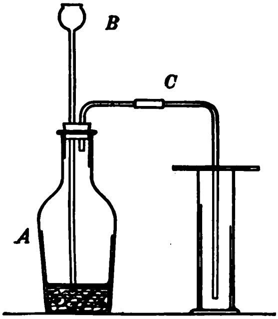


Fig. 70. The preparation of hydrogen sulfide

Chemical conduct. The most important chemical properties of hydrogen sulfide are the following:

1. ***Acid properties.*** When dissolved in water, hydrogen sulfide acts as a weak acid, the solution being sometimes called hydrosulfuric acid. The solution turns blue litmus red, and neutralizes bases, forming salts called *sulfides.*

2. ***Action with oxygen.*** The elements composing hydrogen sulfide have each a strong tendency to combine with oxygen, and are not held together very firmly. Consequently the gas burns readily in oxygen or air according to the equation

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$

When there is not enough oxygen for both the sulfur and the hydrogen, the latter element combines with the oxygen, and the sulfur is set free:

$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S$$

3. ***Reducing action.*** Owing to the ease with which hydrogen sulfide decomposes and the strong tendency of both sulfur and hydrogen to combine with oxygen, the substance is a strong *reducing* agent.

4. ***Action on metals.*** Hydrogen sulfide acts upon many metals, forming *sulfides.* Silver sulfide (Ag_2S) is black, and it is owing to traces of hydrogen sulfide in the air that silver objects tarnish.

Sulfur springs. The waters of many natural springs hold hydrogen sulfide in solution, as is indicated by their strong odor and the way in which they will blacken a silver coin. When the water reaches the air, the hydrogen sulfide is slowly oxidized, with the liberation of sulfur, which often deposits about the borders of the spring.

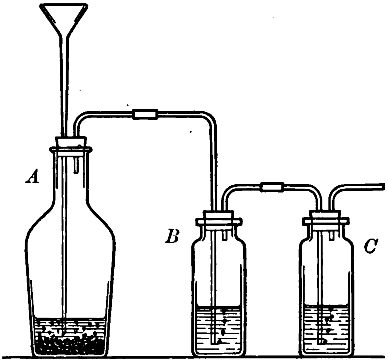


FIG. 71. The preparation of insoluble sulfides

Salts of hydrosulfuric acid; sulfides. The salts of hydrosulfuric acid (called *sulfides*) form an important class of salts. Many of them are found abundantly in nature, and some of them are important ores.

Uses of the sulfides in analysis. Most of the sulfides are insoluble in water, and some of them are insoluble in acids. Consequently, when hydrogen sulfide is passed into a solution of a salt, it often happens that a sulfide is precipitated. With copper chloride the equation is

$$CuCl_2 + H_2S \longrightarrow CuS + 2\,HCl$$

Because of the fact that some metals are precipitated in this way as sulfides while others are not, hydrogen sulfide is extensively used in the separation of the metals in the laboratory.

The sulfides are prepared in the laboratory by passing hydrogen sulfide through solutions of the salts of the metals as shown in Fig. 71. The hydrogen sulfide generated in flask *A*, is passed through bottles *B* and *C*, containing, say, solutions of silver nitrate and arsenic chloride respectively. As the gas bubbles through the solutions there is formed black silver sulfide in *B* and yellow arsenic sulfide in *C*.

OXIDES OF SULFUR

Sulfur forms two well-known compounds with oxygen: sulfur dioxide (SO_2), sometimes called sulfurous anhydride; and sulfur trioxide (SO_3), frequently called sulfuric anhydride.

Sulfur dioxide (SO_2). Sulfur dioxide often occurs in nature in the gases issuing from volcanoes, and in solution in the water of many springs. It is likely to be found wherever sulfur compounds are undergoing oxidation.

Preparation. Two general ways may be mentioned for the preparation of sulfur dioxide:

1. ***By the combustion of sulfur.*** Sulfur dioxide is readily formed when sulfur or certain compounds containing sulfur, such as the metal sulfides, are heated in air or oxygen:

$$S + O_2 \longrightarrow SO_2$$
$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$

2. ***By the reduction of sulfuric acid.*** When concentrated sulfuric acid is heated with certain metals, such as copper, part of the acid is changed into copper sulfate and part is

reduced to sulfurous acid. The latter then decomposes into sulfur dioxide and water, the complete equation being

$$Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2\,H_2O$$

Properties. Sulfur dioxide is a colorless gas, which at ordinary temperatures is 2.2 times as heavy as air. It has a peculiar, irritating odor. The gas is very soluble in water, 1 volume of water dissolving 80 volumes of the gas under standard conditions. It is easily condensed to a colorless liquid, and can be purchased in this condition, stored in strong bottles or in metal cylinders (Fig. 72).

Chemical conduct. Sulfur dioxide has a marked tendency to combine with other substances, and is therefore an active substance chemically. It combines with oxygen gas, but not very easily. It can, however, take oxygen away from some other substances, and is therefore a good reducing agent. Its most marked chemical property is its ability to combine with water.

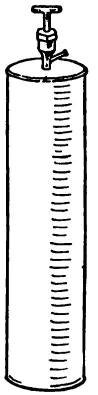


FIG. 72. A cylinder of sulfur dioxide

Sulfurous acid (H_2SO_3). When sulfur dioxide is passed into water, it combines chemically with it to form *sulfurous acid* (H_2SO_3). It is impossible to prepare this acid in pure form, as it breaks down very easily into water and sulfur dioxide. The reaction is therefore reversible, and is expressed by the equation

$$H_2O + SO_2 \rightleftarrows H_2SO_3$$

Solutions of the acid in water are often prepared and have a number of interesting properties and commercial uses.

1. ***Acid properties.*** The solution has all the properties typical of a very weak acid. When neutralized by bases, sulfurous acid yields a series of salts called *sulfites*, most of which are insoluble in water.

2. ***Reducing properties.*** Solutions of sulfurous acid act as good reducing agents. This is due to the fact that sulfurous acid has the power of taking up oxygen from the air or from substances rich in oxygen, and is changed by this reaction into sulfuric acid:

$$2\,H_2SO_3 + O_2 \longrightarrow 2\,H_2SO_4$$

3. ***Bleaching properties.*** Sulfurous acid has strong bleaching properties, acting upon many colored substances in such a way as to destroy their color. It is on this account used to bleach paper, straw goods, and even such foods as canned corn and dried fruits. As a rule the bleaching is not permanent.

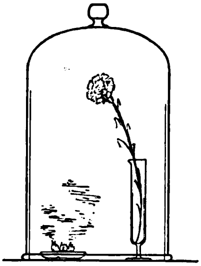


FIG. 73. Bleaching a flower with sulfur dioxide

The bleaching properties of sulfurous acid may be shown by bringing a small dish of burning sulfur under a bell jar (Fig. 73) in which has been placed some highly colored flower moistened with water. Straw hats may be cleaned and brightened in a similar way.

4. ***Antiseptic properties.*** Sulfurous acid has marked antiseptic properties, and on this account has the power of arresting fermentation. It is therefore used in certain foods containing sugars, such as sweet cider, canned corn, and dried fruits, serving not only as a preservative but also as a bleaching agent to remove objectionable colors. Whether or not its use in foods should be permitted, is a much debated question.

Salts of sulfurous acid; sulfites. The sulfites are solid compounds and, like sulfurous acid, have the power of taking up oxygen very readily, and are good reducing agents. On account of this tendency, commercial sulfites are often contaminated with sulphates.

Sulfur trioxide (SO_3). When sulfur dioxide and oxygen are heated together at a rather high temperature, a small amount of sulfur trioxide (SO_3) is formed, but the reaction is slow and incomplete. If, however, the heating takes place in the presence of very fine platinum dust, the reaction is rapid and nearly complete:

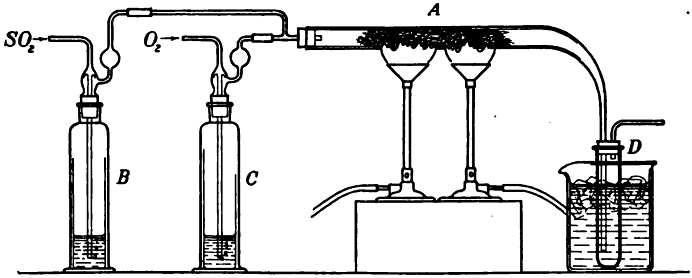


Fig. 74. The preparation of sulfur trioxide

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$

Experimental preparation of sulfur trioxide. The experiment can be performed by the use of the apparatus shown in Fig. 74, the fine platinum being secured by moistening asbestos fiber with a solution of chloroplatinic acid and igniting it in a flame. The fiber, covered with fine platinum, is placed in a tube of hard glass *A*, which is then heated with a burner to about 400°, while sulfur dioxide and air are passed into the tube through the drying bottles *B* and *C*. Union takes place at once, and the strongly fuming sulfur trioxide escapes from the jet at the end of the tube, or it may be condensed by surrounding the receiving tube *D* with a freezing mixture.

Properties of sulfur trioxide. Sulfur trioxide is a colorless liquid which solidifies at about 15° and boils at 46°. A trace of moisture causes it to solidify into a mass of silky white crystals somewhat resembling asbestos fiber in appearance. In contact with the air it fumes strongly, and when thrown upon water it dissolves with a hissing sound and the liberation of a great deal of heat. The product of this reaction is sulfuric acid, so that sulfur trioxide is the *anhydride* of that acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Catalysis. It has been found that many chemical reactions, such as the union of sulfur dioxide with oxygen, are much influenced by the presence of substances which do not themselves seem to take a part in the reaction and are left apparently unchanged after it has ceased. These reactions go on very slowly under ordinary circumstances, *but are greatly hastened* by the presence of the foreign substance. Substances which *increase the speed of reactions* in this way are said to act as *catalytic agents* or *catalyzers*, and the action is called *catalysis.* Just how the action is brought about is not well understood, but the part played by the catalyzer is no doubt different in different cases.

Examples of catalysis. Oxygen and hydrogen combine with each other at ordinary temperatures in the presence of platinum powder, while if no catalytic agent is present, they do not combine in appreciable quantities until a much higher temperature is reached. Potassium chlorate, when heated with manganese dioxide, gives up its oxygen at a much lower temperature than when heated alone (p. 16). Hydrogen dioxide decomposes very rapidly when powdered manganese dioxide is sifted into its concentrated solution. In the Haber process for preparing ammonia, metallic iron promotes the reaction between nitrogen and hydrogen.

On the other hand, the catalytic agent sometimes retards chemical action; for example, a solution of hydrogen dioxide decomposes more slowly when it contains a little phosphoric acid or acetanilide than when perfectly pure. It is probable that many of the chemical transformations in physiological processes, such as digestion, are assisted by certain substances acting as catalytic agents. The principle of catalysis is therefore very important.

Sulfuric acid (oil of vitriol) (H_2SO_4). Sulfuric acid is one of the most important of all manufactured chemicals. Not only is it one of the most common reagents in the laboratory, but enormous quantities of it are used in many of the industries, especially in the refining of petroleum and the manufacture of nitroglycerin, hydrochloric and nitric acids, sodium carbonate, and phosphate fertilizers.

Manufacture of sulfuric acid. Sulfuric acid can be made at low cost, and is the cheapest of the commercial acids. Two general methods are used in its manufacture.

1. ***Contact process.*** In this process sulfur trioxide is made from sulfur dioxide and oxygen, as explained under Fig. 74. The two gases are conducted through iron tubes filled with some porous material, such as asbestos or sodium sulfate, through which is interspersed a suitable catalyzer, such as iron oxide or platinum. The sulfur trioxide so formed reacts with water to form sulfuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

The contact process is only used when the *concentrated* acid is desired.

2. ***Chamber process.*** The older method of manufacture, exclusively employed until recent years and still the most important process, is much more complicated. The conversion of water, sulfur dioxide, and oxygen into sulfuric acid

is accomplished by the *catalytic action* of oxides of nitrogen. Since these oxides are gases, it is difficult to prevent their escape, and very elaborate precautions have to be taken to reduce the loss as much as possible. The reactions are brought about in large, lead-lined chambers, into which oxides of nitrogen, sulfur dioxide, steam, and air are introduced in suitable proportions.

The dilute acid resulting collects upon the floor of the lead chambers. It is drawn off, and in this form serves for many purposes, such as the manufacture of fertilizers. The pure concentrated acid can be prepared from the dilute acid, but the process is costly, so that it sometimes is cheaper to prepare this form of acid by the contact process.

Properties. Pure anhydrous sulfuric acid, more properly termed *hydrogen sulfate*, is a colorless, oily liquid nearly twice as heavy as water. The ordinary concentrated acid contains about 2 per cent of water, has a density of 1.84, and boils at 338°. It is sometimes called *oil of vitriol*, since it was formerly made by distilling a mixture of substances, one of which was called *green vitriol.*

Chemical conduct. Sulfuric acid possesses chemical properties which make it one of the most important of chemical substances.

1. ***Action as an acid.*** In dilute solution sulfuric acid acts as a very strong acid, turning blue litmus red and forming salts with oxides and hydroxides.

2. ***Action as an oxidizing agent.*** Sulfuric acid contains a large percentage of oxygen and is, like nitric acid, a very good oxidizing agent. When the concentrated acid is heated with sulfur or carbon or various other substances, oxidation takes place, the sulfuric acid decomposing according to the equation

$$H_2SO_4 \longrightarrow H_2SO_3 + [O]$$

3. ***Action on metals.*** In *dilute* solution sulfuric acid acts upon many metals, such as zinc, forming a sulfate and liberating hydrogen. When the *concentrated* acid is employed, the first action is one of oxidation. With copper the reaction is represented by the equation

$$Cu + H_2SO_4 \longrightarrow CuO + H_2O + SO_2$$

The copper oxide then dissolves in an additional quantity of sulfuric acid to form copper sulfate:

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

These two equations can be combined into the form

$$Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + 2\,H_2O + SO_2$$

4. ***Action on salts.*** We have repeatedly seen that an acid of high boiling point, heated with the salt of some acid of lower boiling point, will drive out the low-boiling acid (p. 138). The boiling point of sulfuric acid (338°) *is higher than that of almost any common acid;* hence it is largely used in the preparation of other acids.

5. ***Action on water.*** Concentrated sulfuric acid has a very great affinity for water, and is therefore an effective drying, or *dehydrating*, agent. Gases which have no chemical action upon sulfuric acid can be freed from water vapor by bubbling them through the concentrated acid.

Not only can sulfuric acid absorb water, but it will often withdraw the elements hydrogen and oxygen from a compound containing them, decomposing the compound and combining with the water so formed. For this reason most organic substances, such as sugar, wood, cotton and woolen fiber, and even flesh, all of which contain much oxygen and hydrogen in addition to carbon, are charred, or burned, by the action of the concentrated acid.

Salts of sulfuric acid; sulfates. The sulfates form a very important class of salts, and many of them have commercial uses. Copperas (iron sulfate), blue vitriol (copper sulfate), and Epsom salt (magnesium sulfate) serve as examples. Many sulfates are important minerals, prominent among these being gypsum (calcium sulfate) and barite (barium sulfate).

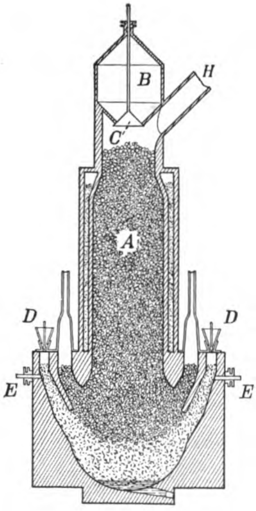


FIG. 75. A furnace for the manufacture of carbon disulfide

Monobasic and dibasic acids. Acids like hydrochloric and nitric acids, which have only one replaceable hydrogen atom in the molecule, or, in other words, which yield one hydrogen ion in solution, are called *monobasic* acids. Acids yielding two hydrogen ions in solution are called *dibasic* acids. Similarly, we may have *tribasic* and *tetrabasic* acids. The three acids of sulfur are dibasic acids.

Normal and acid salts. It is possible for such acids as H_2S, H_2SO_3, H_2SO_4, to form two kinds of salts. In the one all of the hydrogen of the acid has been replaced by a metal, as in the salts Na_2S and Na_2SO_4. These are called *normal* salts. In the other only one half of the hydrogen has been replaced, as in the salts $NaHS$ and $NaHSO_4$. These are called *acid* salts, since they are at once both salts and acids. Acid salts are often designated by the prefix *bi-*; thus, $NaHSO_4$ is called sodium acid sulfate, sodium hydrogen sulfate, or sodium bisulfate.

Carbon disulfide (CS_2). When sulfur vapor is passed over highly heated carbon the two elements combine, forming *carbon disulfide* (CS_2), just as oxygen and carbon unite to form carbon dioxide (CO_2). The substance is a heavy, colorless liquid, possessing, when pure, a pleasant, ethereal odor. On standing for some time, especially when exposed to sunlight, it undergoes a slight decomposition and acquires a most disagreeable odor. It is a very good solvent for many substances, such as gums, resins, waxes, and fats, which are insoluble in most liquids. It boils at a low temperature (46°), and its vapor is not only very poisonous but inflammable as well. It burns in the air to form carbon dioxide and sulfur dioxide. It is prepared in considerable quantities for use as a solvent and as an insecticide.

Commercially, carbon disulfide is made by the direct combination of carbon and sulfur, the heat necessary for this union being derived from an electric current. The main part of a large furnace (Fig. 75, *A*) is filled with charcoal introduced through the trap *C*. Sulfur is added through the hoppers *D, D*. An electric current is passed in at *E, E*. The heat generated is sufficient to vaporize the sulfur, which then unites with the hot carbon to form carbon disulfide. The vapors escape at *H* and are condensed. Some of the furnaces are 40 ft. in height and yield as much as 25,000 lb. of the disulfide in twenty-four hours.

EXERCISES

1. Would the same amount of sulfur dioxide be formed by the combustion of 1 g. of each of the modifications of sulfur?

2. Is the equation for the preparation of hydrogen sulfide a reversible one? As ordinarily carried out, does the reaction complete itself?

3. Suppose that hydrogen sulfide were a liquid, would it be necessary to modify the method of preparation?

4. Does perfectly dry hydrogen sulfide change the color of litmus paper? State reason for your answer.

5. What is an acid anhydride? Aside from those of sulfur, what others have been mentioned?

6. How would you expect dilute sulfuric acid to act upon iron? upon silver? (Refer to displacement series.)

7. Can you suggest a reason for silver spoons becoming tarnished when in contact with certain kinds of food?

8. Mention other instances of catalysis aside from those given in this chapter.

9. In the commercial preparation of carbon disulfide, what is the function of the electric current?

10. How many pounds of sulfur would be necessary in the preparation of 100 lb. of 98 per cent sulfuric acid? *Ans.* 32.07 g.

TOPICS FOR THEMES

The mining of sulfur (see encyclopedia).

Goodyear and his discovery of the method for vulcanizing rubber (see encyclopedia).

The value of spraying fruit trees. (Write to the director of your experiment station for information.)

CHAPTER XVIII

THE PERIODIC LAW

A number of the elements have now been studied somewhat closely. The first three of these, oxygen, hydrogen, and nitrogen, while having some properties in common with each other, have almost no point of similarity as regards their chemical conduct. On the other hand, oxygen and sulfur, while quite different physically, have much in common in the way they act toward other chemicals.

About eighty elements are now known. If all of these should have properties as diverse as do oxygen, hydrogen, and nitrogen, the study of chemistry would plainly be very difficult and complicated. Fortunately a study of the elements shows that certain ones resemble each other more or less closely, so that it is possible to divide them into groups and then study the group as a whole. A number of different methods of classifying the elements have been suggested, but that advanced in 1869 by the Russian chemist Mendeléeff (Fig. 76) has proved the most fruitful. In accordance with this method, the elements are arranged in groups or periods, according to their atomic weights.

The periodic grouping. The general arrangement suggested by Mendeléeff and extended so as to include elements more recently discovered is as follows: Omitting hydrogen, which has the smallest atomic weight, and beginning with helium, which has an atomic weight of 3.99, the succeeding seven elements are arranged in a horizontal row in the order of their atomic weights, as given below. These eight elements all differ markedly from each other, but the one having the next highest atomic weight, neon, is very similar to helium. It is placed just under helium, and a new horizontal row follows as shown below. The next element, argon, resembles helium and neon and begins a third row.

He (3.99)	Li (6.94)	Gl (9.1)	B (11)	C (12)	N (14.01)	O (16)	F (19)
Ne (20.2)	Na (23)	Mg (24.32)	Al (27.1)	Si (28.3)	P [illegible])	S (32.07)	Cl (35.46)
A (39.88)	K (39.1)	Ca (40.07)	Sc (44.1)	Ti (48.1)	V (51)	Cr (52)	Mn (54.93)

If now we consider the elements that fall under each other in these three rows, a remarkable fact is brought to light. Not only is there a strong similarity between helium, neon, and argon, which form the first vertical column, but the elements in the other columns exhibit much of the same kind of similarity among themselves, and evidently form natural groups.

Iron, nickel, and cobalt, following manganese, have atomic weights near together, and are very similar chemically. They do not strongly resemble any of the elements so far considered, and so are placed in a group by themselves. The first three horizontal rows of the table (p. 161) shows the arrangement of these twenty-seven elements. A new horizontal row is begun with copper.

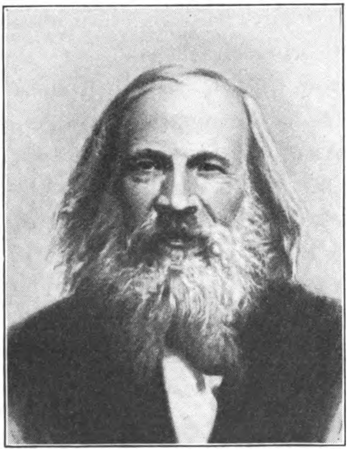


FIG. 76. Mendeléeff (1834–1907)

A famous Russian chemist, who first proposed the periodic classification of the elements

THE PERIODIC ARRANGEMENT OF THE ELEMENTS

PERIODS	GROUP 0		GROUP I		GROUP II		GROUP III		GROUP IV		GROUP V		GROUP VI		GROUP VII		GROUP VIII
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	
1	He = 3.99		Li = 6.94		Gl = 9.1		B = 11		C = 12		N = 14.01		O = 16		F = 19		
2		Ne = 20.2		Na = 23		Mg = 24.32		Al = 27.1		Si = 28.3		P = 31.04		S = 32.07		Cl = 35.46	
3	A = 39.88		K = 39.1		Ca = 40.07		Sc = 44.1		Ti = 48.1		V = 51		Cr = 52		Mn = 54.93		Fe = 55.84 Ni = 58.68 Co = 58.97
4				Cu = 63.57		Zn = 65.37		Ga = 69.9		Ge = 72.5		As = 74.96		Se = 79.2		Br = 79.92	
5	Kr = 82.92		Rb = 85.45		Sr = 87.63		Y = 89		Zr = 90.6		Cb = 93.5		Mo = 96				Ru = 101.7 Rh = 102.9 Pd = 106.7
6				Ag = 107.88		Cd = 112.4		In = 114.8		Sn = 119		Sb = 120.2		Te = 127.5		I = 126.92	
7	X = 130.2		Cs = 132.81		Ba = 137.37		La = 139		Ce-Yb* 140.25-172		Ta = 181.5		W = 184				Os = 190.9 Ir = 193.1 Pt = 195.2
8				Au = 197.2		Hg = 200.6		Tl = 204		Pb = 207.1		Bi = 208					
9	Nt = 222.4				Ra = 226.4				Th = 232.4		U = 238.5						
Formula of oxide Formula of hydride			R_2O RH		RO RH_2		R_2O_3 RH_3		RO_2 RH_4		R_2O_5 RH_3		RO_3 RH_2		R_2O_7 RH		RO_4

* This includes a number of elements whose atomic weights lie between 140 and 173, but which have not been accurately studied, and so their proper arrangement is uncertain.

Following the fifth and seventh rows are groups of three closely related elements, so the completed arrangement has the appearance represented in the table.

The relation of properties of elements to atomic weights. There is evidently a close relation between the properties of an element and its atomic weight. For example, consider the elements in the first horizontal row. Helium is an inert element. Following it, lithium is a metallic element, has a valence of 1, and possesses a strong base-forming character. The next element, glucinum, has a valence of 2, and is less strongly base-forming, while boron has some base-forming and some acid-forming properties. In carbon, all base-forming properties have disappeared, and the acid-forming properties are more marked than in boron. These become still more emphasized as we pass through nitrogen and oxygen, until on reaching fluorine we have one of the strongest acid-forming elements. The properties of these eight elements vary regularly with their atomic weights, or, in mathematical language, are *regular functions* of them.

The periodic law. If it were true that helium had the smallest atomic weight of any of the elements and fluorine the greatest, so that in passing from one to the other we included all the elements, we could say that the properties of elements were *continuous* functions of their atomic weights. But fluorine is an element of relatively small atomic weight, and the one following it, neon, breaks the regular order, for in it reappear all the characteristic properties of helium. Sodium, following neon, bears much the same relation to lithium that neon does to helium, and the properties of the elements in the second row vary much as the properties of the elements in the first row did, until argon is reached, when another repetition begins. The properties of the elements do not vary continuously, therefore, with atomic weights, but at regular intervals there is a repetition, or *period.* This generalization is known as the *periodic law,* and may be stated thus: *The properties of elements are periodic functions of their atomic weights.*

Two families in a group. The elements of each group (excepting Group 0) falls naturally into two families. The elements in the odd-numbered horizontal rows, or periods, form one family, those in the even-numbered periods, the other. In the table these are arranged under the headings *A* and *B*. The elements in one family are much more similar to each other than they are to those in the other family in the same group. Thus, magnesium, zinc, cadmium, and mercury form one family of very similar elements in Group II, while calcium, strontium, barium, and radium form the other.

Family resemblances. Let us inquire more closely in what respects the elements of a family resemble each other.

1. ***Valence.*** In general the valence of the elements in a family is the same, and the formulas of their compounds are therefore similar. The formulas R_2O, RO, etc., placed below the columns, represent the oxides of the elements in the column, while the formulas RH, RH_2, etc. represent the hydrides or chlorides.

2. ***Chemical conduct.*** The chemical characteristics of the members of a family are somewhat similar. If one member is a metal, the others usually are; if one is a nonmetal, so, too, are the others. There is also a certain regularity in the properties of the elements in each family. If the one element at the head of the family is a strong acid-forming element, this characteristic is likely to diminish gradually as we pass to the members of the family having higher atomic weights. Thus, phosphorus is strongly acid-forming, arsenic less so, and antimony still less so, while bismuth has almost no acid-forming properties.

3. ***Physical properties.*** In the same way, the physical properties of the members of a family are in general somewhat similar, and show a regular gradation as we pass from element to element in the family. Thus, the densities of the members of the magnesium family increase with their atomic weights, while their melting points decrease (p. 313).

Value of the periodic law. The periodic law has proved of much value in the development of the science of chemistry.

1. ***It simplifies study.*** It is at once evident that such regularities very much simplify the study of chemistry. A thorough study of one element of a family makes the study of the other members a much easier task.

2. ***It suggests the probable existence of new elements.*** When the periodic law was first formulated there were a number of vacant places in the table which evidently belonged to elements at that time unknown. From their position in the table, Mendeléeff predicted with great precision the properties of the elements which he felt sure would one day be discovered to fill these places. Three of them, scandium, germanium, and gallium, were found within fifteen years, and their properties agreed in a remarkable way with the predictions of Mendeléeff.

This is shown in the following table, in which the properties of gallium are compared with those which Mendeléeff predicted:

PROPERTIES OF GALLIUM	PREDICTED	FOUND
Atomic weight	about 69	69.9
Melting point	low	30.2°
Specific gravity	5.9	5.95
Formula of oxide	X_2O_3	Ga_2O_3
[illegible] of air	no action	only slight, even at red heat

3. ***It indicates probable errors.*** The physical constants of many of the elements did not at first agree with those suggested by the periodic law, and a further study of many such cases showed that errors had been made.

Imperfections of the law. There still remain a good many features which must be regarded as imperfections in the law. Most conspicuous is the fact that the element hydrogen has no place in the table. Moreover, according to their atomic weights, tellurium should follow iodine, and argon should follow potassium, but their properties show in each case that this order must be reversed. The table separates some elements altogether which in many respects have closely agreeing properties. Iron, chromium, and manganese, although they are similar in many respects, are all in different groups.

The periodic law is therefore to be regarded as but a partial and imperfect expression of some very important and fundamental relation between the substances which we know as elements, the exact nature of this relation being as yet not completely clear to us.

EXERCISES

1. Suppose that an element were discovered that filled the blank in Group 0, Period 4; what properties would it probably have?

2. Sulfur and oxygen both belong to the same group; in what respects are they similar?

TOPIC FOR THEMES

Mendeléeff (Thorpe, Essays in Historical Chemistry).

CHAPTER XIX

THE CHLORINE FAMILY

NAME	ATOMIC WEIGHT	MELTING POINT	BOILING POINT	COLOR AND STATE
Fluorine (F) . .	19.00	−223°	− 187°	Pale-yellowish gas
Chlorine (Cl) . .	35.46	−101.5°	− 33.6°	Greenish-yellow gas
Bromine (Br) . .	79.92	− 7.3°	63°	Red liquid
Iodine (I) . . .	126.92	113.5°	184.4°	Purplish-black solid

The family. The four elements named in the above table form a strongly marked family, and illustrate very clearly the way in which the members of a family in a periodic group resemble each other, as well as the character of the differences which we may expect to find between the individual members. The elements constituting the family are often termed the *halogens.* They will be described in the order of their atomic weights.

FLUORINE

Occurrence. Fluorine occurs in nature most abundantly in the mineral fluorite (CaF_2), in cryolite (Na_3AlF_6), and in the complex mineral fluorapatite ($3\,Ca_3(PO_4)_2 \cdot CaF_2$).

Preparation. Because of its great activity, the element is difficult to liberate from its compounds. Its preparation was finally accomplished in 1886 by the French chemist Moissan (Fig. 77) by the electrolysis of hydrogen fluoride. His success was due to his observation that liquid hydrogen fluoride (H_2F_2) in which is dissolved a little potassium acid fluoride (KHF_2) is a good electrolyte. The electrolyte was placed in a U-shaped tube made of platinum (or copper) upon which fluorine has little action. This tube was furnished with electrodes and delivery tubes as shown in Fig. 78. When the solution was electrolyzed, hydrogen was set free at the cathode, and fluorine at the anode.

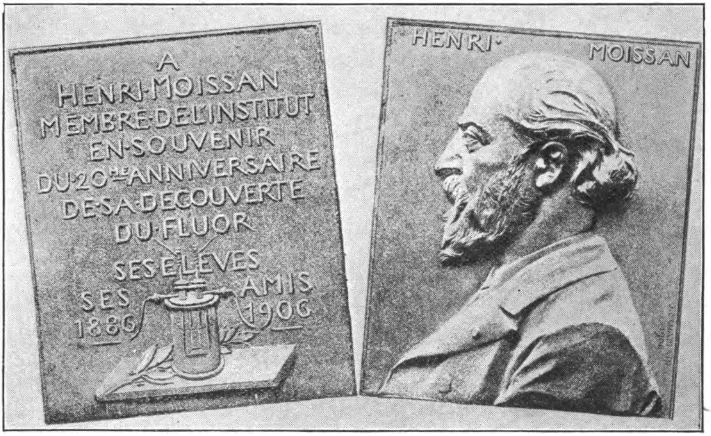


FIG. 77. Tablet erected by the associates and friends of Moissan, in his laboratory in Paris, in 1906, on the twentieth anniversary of the isolation of fluorine

Properties and conduct. Fluorine is a gas of slightly yellowish color and is very difficult to liquefy. It is the most active of all the elements at ordinary temperatures, and combines with all the common elements save oxygen, very often with incandescence. It has a particularly strong affinity for hydrogen, and is able to withdraw it from any of its compounds with other elements, forming hydrogen fluoride. It is extremely poisonous.

Hydrogen fluoride (H_2F_2). Hydrogen fluoride is readily obtained from fluorite by the action of concentrated sulfuric acid. The equation is as follows:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2$$

In its properties hydrogen fluoride resembles the hydrides of the other elements of this family, being, however, more easily condensed to a liquid. It boils at 19.4°, and can therefore be liquefied at ordinary pressures. It is soluble in all proportions in water, forming *hydrofluoric acid.* Its fumes are exceedingly irritating to the respiratory organs, and several chemists have lost their lives by accidentally breathing them.

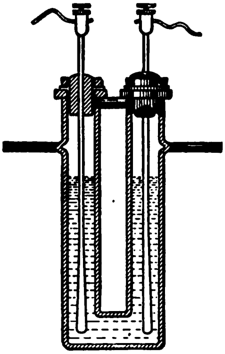


FIG. 78. Apparatus for the preparation of fluorine

Hydrofluoric acid. Hydrofluoric acid, like other strong acids, readily acts on bases and metallic oxides, and forms the corresponding *fluorides.* It acts very vigorously upon organic matter, a single drop of the concentrated acid making a sore on the skin which is slow in healing and very painful. Its most characteristic property is its action upon silicon dioxide (SiO_2), with which it forms water and the gas silicon tetrafluoride (SiF_4), as shown in the equation

$$SiO_2 + 2\,H_2F_2 \longrightarrow SiF_4 + 2\,H_2O$$

Glass consists of certain compounds of silicon which are likewise acted on by the acid, so that it cannot be kept in glass bottles. It is preserved in flasks made of a wax derived from petroleum and known as ceresin.

Etching. Advantage is taken of this reaction in etching designs upon glass. The glass vessel is painted over with a protective paint upon which the acid will not act, the parts which it is desired to make opaque being left unprotected. A mixture of fluorite and sulfuric acid is then painted over the vessel, and after a few minutes the vessel is washed clean. Wherever the hydrofluoric acid comes in contact with the glass it acts upon it, destroying its luster and making it opaque, so that the exposed design will be etched upon the clear glass. Frosted glass globes are often made in this way, but more frequently by a sand blast.

The etching may also be effected by covering the glass with a thin layer of paraffin, cutting the design through the wax and then exposing the glass to the fumes of the gas.

CHLORINE

Historical. While studying the action of hydrochloric acid upon the mineral pyrolusite, the Swedish chemist, Scheele, in 1774, obtained a yellowish gaseous substance to which he gave a name in keeping with the phlogiston theory then current (p. 6). Later it was supposed to be a compound containing oxygen. In 1810, however, the English chemist, Sir Humphry Davy, proved it to be an element and named it *chlorine.*

Occurrence. Chlorine does not occur free in nature, but its compounds are widely distributed. It is found in combination with the metals in the form of *chlorides*, those of sodium, magnesium, and potassium being the most abundant. All salt water contains these substances, particularly sodium chloride (common salt), and very large salt beds of chlorides are found in many parts of the world.

Preparation. Two general methods of preparing chlorine may be mentioned, one of which is the usual laboratory method, while the other is the commercial method.

1. ***Laboratory method.*** In the laboratory, chlorine is easily made by warming the mineral pyrolusite (manganese dioxide, MnO_2) with concentrated hydrochloric acid. The first reaction, which is similar to the action of acids upon oxides in general, is expressed in the equation

$$MnO_2 + 4\,HCl \longrightarrow MnCl_4 + 2\,H_2O$$

The manganese compound so formed is very unstable, however, and breaks down according to the equation

$$MnCl_4 \longrightarrow MnCl_2 + Cl_2$$

Instead of using hydrochloric acid in the preparation of chlorine, it serves just as well to use a mixture of sodium chloride and sulfuric acid, since these two react to form hydrochloric acid. In this case the complete reaction is expressed by the equation

$$2\,NaCl + MnO_2 + 2\,H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + Cl_2$$

The manganese dioxide and the hydrochloric acid are brought together in a flask *A* (Fig. 79), and a gentle heat is applied. The chlorine set free passes out through *B*, bubbles through a little water in *C* (which removes any hydrogen chloride carried over with it), and finally through some sulfuric acid in *D*, which dries the gas. Being somewhat soluble in water, it is collected in cylinder *E* by displacement of air, the color showing when the cylinder is full.

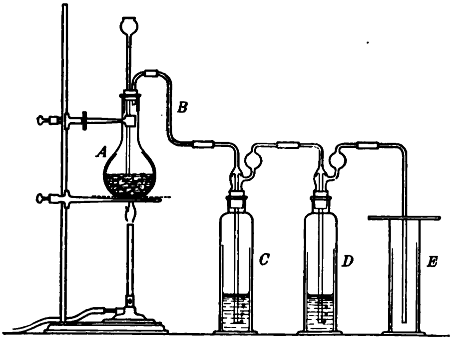


FIG. 79. The preparation of pure chlorine

2. ***Commercial method.*** It will be recalled that when a solution of sodium chloride is electrolyzed, chlorine is evolved at the anode, while sodium hydroxide is formed at the cathode and remains in solution (p. 104). All of the chlorine prepared for commercial purposes in the United States is obtained in this way. The method has advantages in that sodium chloride is cheap and that the sodium hydroxide formed in the process has many commercial uses. The chlorine so obtained is either compressed in strong iron cylinders and shipped in this form or is passed into slaked lime forming the solid known as *chloride of lime* or *bleaching powder* (p. 303), which can be easily shipped and from which the chlorine can be recovered as needed.

Properties. Chlorine is a greenish-yellow gas which has a peculiar, suffocating odor and produces a very irritating effect upon the throat and lungs. Even when inhaled in small quantities, it often produces all the symptoms of a very hard cold, and in larger quantities may have serious and even fatal effects. Inhaling ether or ammonia gives some relief. Chlorine is nearly 2.5 times as heavy as air, and can therefore be collected by displacement of air. One volume of water under ordinary conditions dissolves about 3 volumes of chlorine.

Chemical conduct. At ordinary temperatures chlorine is far more active chemically than any of the elements we have so far considered, with the exception of fluorine; indeed, it is one of the most active of all elements.

1. ***Action on elements.*** A great many elements combine directly with chlorine, especially when hot. A strip of copper foil heated in a burner flame and then dropped into chlorine burns with incandescence. Antimony and arsenic in the form of a fine powder at once burst into flame when dropped into jars of chlorine. The products formed in all cases where chlorine combines with another element are called *chlorides.*

2. ***Action on hydrogen.*** Chlorine has a particularly strong affinity for hydrogen, uniting with it to form hydrogen chloride. A jet of hydrogen burning in the air continues to burn when introduced into a jar of chlorine *A* (Fig. 80), giving a somewhat luminous flame. A mixture of the two gases explodes violently when a spark is passed through it or when it is exposed to bright sunlight.

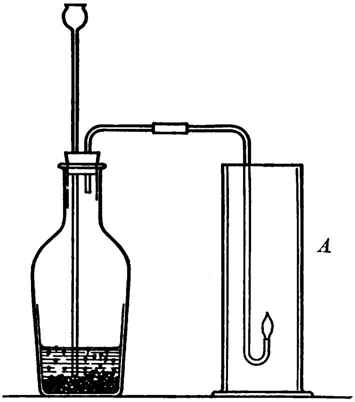


FIG. 80. Burning hydrogen in chlorine

3. ***Action on substances containing hydrogen.*** Not only will chlorine combine directly with free hydrogen but it will often abstract the element from its compounds. Thus, when chlorine is passed into a solution containing hydrogen sulfide, sulfur is precipitated and hydrochloric acid formed. The reaction is shown by the following equation:

$$H_2S + Cl_2 \longrightarrow 2\,HCl + S$$

Even water, which is a very stable compound, can be decomposed by chlorine, the oxygen being liberated. This may be shown in the following way:

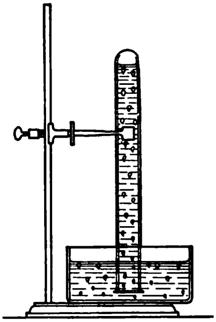


FIG. 81. The action of chlorine on water in the sunlight

Action of chlorine on water. A long tube of rather large diameter is filled with a concentrated solution of chlorine in water and inverted in a vessel of the same solution, as shown in Fig. 81, and the apparatus is placed in bright sunlight. Very soon bubbles of a gas will be observed to rise through the solution and collect in the tube, and an examination of this gas will show that it is oxygen. It is liberated from water in accordance with the following equation:

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

4. ***Action on color substances; bleaching action.*** If strips of brightly colored cloth or some highly colored flowers are placed in dry chlorine, no marked change in color is noticed, as a rule. If, however, the cloth and flowers are first moistened, the color rapidly disappears, or, in other words, the objects are *bleached.* Evidently the moisture as well as the chlorine is concerned in the action. A study of the case shows that the chlorine combines with the hydrogen of the water, and the oxygen set free oxidizes the color substance, converting it into a colorless compound. It is evident from this explanation that chlorine will bleach only those substances which are changed into colorless compounds by oxidation.

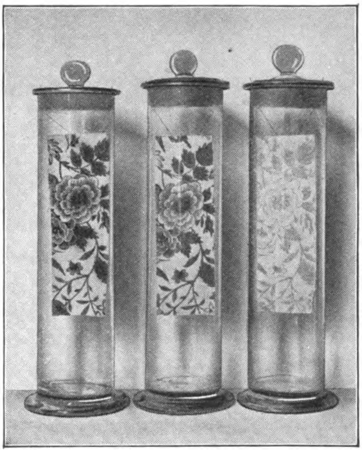


FIG. 82. The bleaching action of moist chlorine

Fig. 82 illustrates the bleaching action of chlorine. Strips from the same piece of cloth are suspended in three jars, of which the first contains air, the second *dry* chlorine, and the third *moist* chlorine. It will be noted that dry chlorine has almost no bleaching action, while the moist chlorine has partially removed the color.

5. ***Action as a disinfectant.*** Chlorine has also marked germicidal properties, and the free element, as well as compounds from which it is easily liberated, are used as disinfectants. It is also used to destroy the microörganisms in city water supplies.

Bleaching. The process known as bleaching is an important one in connection with many industries. Thus, the various kinds of fabrics woven from vegetable fibers, such as flax and cotton, are always more or less colored ; hence bleaching is necessary if a white fabric is desired. This was formerly accomplished by spreading the cloth on plots of grass and exposing it to the action of air and sunlight, but the process was very slow. The same results are now obtained in a short time by the use of chlorine.

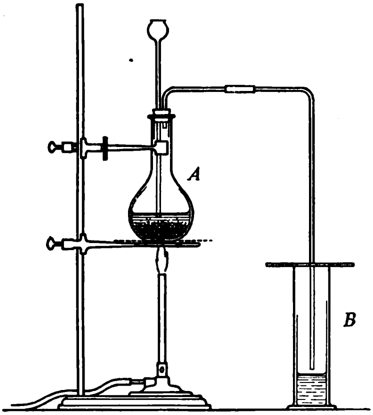


Fig. 83. Laboratory preparation of hydrogen chloride

Certain foods, such as dried fruits (p. 150) and the lower grades of flour, are also bleached. The bleaching of flour was formerly prohibited, but is now largely practiced, since it makes the product white.

Other bleaching agents. While chlorine is the bleaching agent most generally used, a number of other substances, such as sulfurous acid, hydrogen dioxide, nitrogen dioxide, and ozone, are sometimes employed. Chlorine injures some fabrics, such as silk and straw goods, and in such cases sulfurous acid is used. Flour is bleached either by chlorine or by nitrogen dioxide, a very small amount sufficing to remove the color.

Nascent state. It will be noticed that when oxygen is set free from water by chlorine, it is at that instant able to do what ordinary oxygen gas cannot do, for it bleaches substances which would remain unchanged in dry air or pure oxygen. It is generally true that the activity of an element is greatest at the instant of its liberation from its compounds. To express this fact, elements at the instant of liberation are said to be in the *nascent state.* When moist chlorine acts as a bleaching agent, it is nascent oxygen which does the bleaching.

Hydrogen chloride (HCl). The preparation of this gas may be discussed under two general heads:

1. ***Laboratory preparation.*** While hydrogen chloride (in solution known as *hydrochloric acid*) can be prepared by burning hydrogen in chlorine, it is much more conveniently obtained by treating common salt (sodium chloride) with sulfuric acid. The following equation shows the reaction:

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl$$

The dry salt is placed in the flask *A* (Fig. 83), sulfuric acid is added, and the flask gently warmed. The hydrogen chloride is rapidly given off, and can be collected by displacement of air. To prepare a solution of the gas, the end of the delivery tube is fixed just above the level of some water in the cylinder *B*. The gas is very soluble, and is absorbed as fast as it escapes from the tube.

2. ***Commercial preparation.*** Commercially, hydrogen chloride is prepared in connection with the manufacture of sodium sulfate, the reaction being the same as that just given. It is also prepared by heating sodium hydrogen sulfate (which is obtained in the manufacture of nitric acid) (p. 128) and sodium chloride:

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl$$

In either case the hydrogen chloride liberated is passed into water, in which it dissolves, the solution forming the hydrochloric acid of commerce. When the materials are pure, a colorless solution is obtained. The most concentrated solution has a density of about 1.2 and contains approximately 40 per cent of hydrogen chloride. The commercial acid (often called *muriatic acid*) is usually colored yellow by impurities.

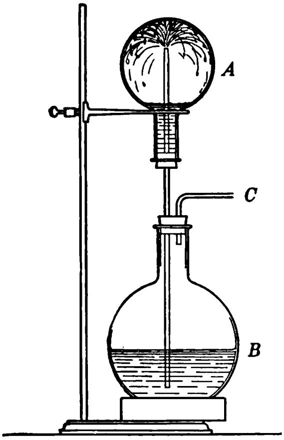


FIG. 84. The hydrogen chloride fountain illustrating the solubility of the gas

Composition of hydrogen chloride. When measured volumes of hydrogen and chlorine are caused to unite, it is found that *1 volume of hydrogen combines with 1 volume of chlorine.* Other experiments show that the volume of hydrogen chloride formed is just equal to the sum of the volumes of hydrogen and chlorine. Therefore *1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride.* Since chlorine is 35.24 times as heavy as hydrogen, it follows that 1 part of hydrogen by weight combines with 35.24 parts of chlorine to form 36.24 parts of hydrogen chloride.

Properties. Hydrogen chloride is a colorless gas which has an irritating effect when inhaled, but no marked odor. It is heavier than air and is very soluble in water. Under standard conditions, 1 volume of water dissolves about 500 volumes of the gas. On warming such a solution, the gas escapes until, at the boiling point, the solution contains about 20 per cent by weight of HCl. Further boiling will not drive out any more acid, but the solution will distill with unchanged concentration. A more dilute solution than this will lose water on boiling until it has reached the same concentration, 20 per cent, and will then distill unchanged.

The extreme solubility of hydrogen chloride in water may be shown as follows: A perfectly dry flask *A* (Fig. 84) is filled with hydrogen chloride. This flask is connected, by means of a glass tube, with a similar flask *B*, which is nearly filled with water, as shown in the figure. The end of the tube opening into flask *A* is drawn out to a rather fine jet. By blowing into the tube *C*, a few drops of water are forced into *A*. Some of the hydrogen chloride at once dissolves, thus diminishing the pressure inside the flask. The water then flows continuously from *B* into *A*, until nearly all the hydrogen chloride is absorbed. It is evident that the connection must be air-tight. The experiment is more striking if the water in *B* is first colored deep blue with litmus.

Chemical conduct. The most important chemical characteristics of hydrogen chloride are the following:

1. ***Action as an acid.*** Its aqueous solution (hydrochloric acid) is a very strong acid; indeed, it is one of the strongest acids known, and has many commercial uses. This acid acts upon oxides and hydroxides, converting them into salts:

$$CuO + 2\,HCl \longrightarrow CuCl_2 + H_2O$$
$$NaOH + HCl \longrightarrow NaCl + H_2O$$

It acts upon many metals, forming chlorides and liberating hydrogen:

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$
$$2\,Al + 6\,HCl \longrightarrow 2\,AlCl_3 + 3\,H_2$$

2. ***Action on oxidizing agents.*** Many oxidizing agents act upon hydrogen chloride as expressed in the following equation:

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

The hydrogen combines with oxygen, liberating chlorine.

Aqua regia. Since nitric acid is a good oxidizing agent, we might expect it to liberate chlorine from hydrogen chloride, and this is found to be the case. A mixture of 1 part of nitric acid and 3 parts of hydrochloric acid is called *aqua regia*, and is one of the strongest solvents known. It owes its solvent powers not to its acid properties but to the nascent chlorine which it liberates. Metals such as gold and platinum, which are not soluble in any of the common acids, readily dissolve in aqua regia, being converted into chlorides by the nascent chlorine.

Salts of hydrochloric acid; chlorides. The chlorides of all the metals are known, and many of them, such as sodium chloride, are very important compounds. With very few exceptions they are solids, and all are soluble in water except silver chloride, lead chloride, and mercurous chloride.

Compounds of chlorine with oxygen and hydrogen. Chlorine combines with oxygen and hydrogen to form four different acids. They are all quite unstable, and most of them cannot be prepared in pure form. Their salts can easily be made, however, and some of them will be met with in the study of the metals. The formulas and names of these acids are as follows:

$HClO$	hypochlorous acid
$HClO_2$	chlorous acid
$HClO_3$	chloric acid
$HClO_4$	perchloric acid

BROMINE

Historical. Bromine was discovered in 1826 by the French chemist Ballard, who isolated it from sea salt. He named it *bromine* ("stench") because of its bad odor.

Occurrence. Bromine occurs almost entirely in the form of bromides, especially as sodium bromide and magnesium bromide, which are found in many salt springs and salt deposits.

The Stassfurt deposits in Germany (p. 286) and the salt waters of Ohio and Michigan are especially rich in bromides.

Preparation of bromine. The laboratory method of preparing bromine is essentially different from the commercial.

1. ***Laboratory method.*** As in the case of chlorine, bromine can be prepared by the action of hydrobromic acid (HBr) on manganese dioxide. Since hydrobromic acid is not a common article of commerce, a mixture of sulfuric acid and a bromide is commonly substituted for it. The materials are placed in a retort *A*, arranged as shown in Fig. 85. The end of the retort comes close to the surface of the water in the flask *B*, which is partially immersed in ice water. On heating, the bromine distills over, and is collected in the cold receiver. The equation is

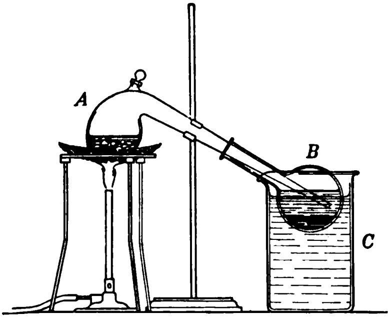


FIG. 85. The preparation of bromine in the laboratory

$$2\,NaBr + 2\,H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + Br_2$$

2. ***Commercial method.*** Bromine is prepared commercially from the waters of salt wells which are especially rich in bromides. On passing a current of electricity through such waters, the bromine is first liberated. Any chlorine liberated, however, will assist in the reaction, since free chlorine decomposes bromides, as shown in the equation

$$2\,NaBr + Cl_2 \longrightarrow 2\,NaCl + Br_2$$

When the water containing the bromine is heated, the liberated bromine distills over into the receiver.

Properties. Bromine is a dark-reddish-brown liquid about 3 times as heavy as water; but even at ordinary temperatures it evaporates rapidly, forming a reddish-brown gas very similar to nitrogen dioxide in appearance. Its vapor has a very offensive odor and is most irritating to the eyes and throat. Bromine is somewhat soluble in water, 100 volumes of water under ordinary conditions dissolving 1 volume of the liquid. It is readily soluble in carbon disulfide, forming a reddish solution.

Chemical conduct and uses. In chemical action bromine is very similar to chlorine. It combines directly with many of the same elements with which chlorine unites, but with less energy. It combines with hydrogen, and takes away the latter element from some of its compounds, but not so readily as does chlorine. Its bleaching properties are also less marked than those of chlorine.

Bromine finds many uses in the manufacture of organic drugs and dyestuffs and in the preparation of bromides. Silver bromide is extensively used in photography, and the bromides of sodium and potassium are used as drugs.

Hydrogen bromide (HBr). When sulfuric acid acts upon a bromide, hydrogen bromide is set free:

$$2\,NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HBr$$

At the same time, some bromine is liberated, as may be seen from the red fumes which appear, and from the odor. The explanation of this is found in the fact that hydrogen bromide is much *less stable* than hydrogen chloride and is therefore *more easily oxidized.* Concentrated sulfuric acid is a good oxidizing agent (p. 154), and oxidizes a part of the hydrogen bromide, liberating bromine:

$$H_2SO_4 + 2\,HBr \longrightarrow 2\,H_2O + SO_2 + Br_2$$

The pure compound is best prepared by adding water to phosphorus tribromide:

$$PBr_3 + 3\,H_2O \longrightarrow 3\,HBr + P(OH)_3$$

Properties. Hydrogen bromide very strikingly resembles hydrogen chloride in physical and chemical properties. The chief point in which it differs from hydrogen chloride is in the fact that it is much more easily oxidized, so that bromine is more readily set free from it than chlorine is from hydrogen chloride. A solution of hydrogen bromide in water is called *hydrobromic acid.* The salts of hydrobromic acid are known as *bromides.* They resemble the chlorides in their properties.

IODINE

Historical. Iodine was discovered in 1812 by Courtois, in the ashes of certain sea plants. Its presence was revealed by its beautiful violet vapor.

Occurrence. Like all the other elements of the chlorine family it is not found in the free state. In the combined state it occurs in very small quantities in sea water, from which it is absorbed by certain sea plants, so that it is found in their ashes. It occurs along with bromine in salt deposits, and is also found in Chile as a constituent of the enormous deposits of sodium nitrate (Chile saltpeter).

Preparation. In the laboratory, iodine can readily be prepared from an iodide by the method used in preparing bromine, sodium iodide being substituted for sodium bromide.

To some extent iodine is prepared commercially by burning seaweed (kelp) at a low temperature, the iodine being left in the ashes as sodium iodide, from which it is easily obtained. Chile saltpeter contains a very small percentage of compounds of iodine, and most of the iodine of commerce comes from the liquors obtained in the purifying of this material.

Properties. Iodine is a purplish-black, shining, heavy solid which crystallizes in brilliant plates. Even at ordinary temperatures it gives off a beautiful violet vapor, which increases in amount as heat is applied. It is only slightly soluble in water, but readily dissolves in alcohol, forming a brown solution (*tincture of iodine*), and in carbon disulfide, forming a violet solution. The element has a strong, unpleasant odor, by no means so irritating as that of chlorine or bromine.

Chemical conduct. Chemically, iodine is quite similar to chlorine and bromine, but is still less active than bromine. Both chlorine and bromine displace it from its salts:

$$2\,KI + Br_2 \longrightarrow 2\,KBr + I_2$$
$$2\,KI + Cl_2 \longrightarrow 2\,KCl + I_2$$

When even minute traces of iodine are added to thin starch paste a very intense blue color develops, and this reaction forms a delicate test for iodine. Iodine is extensively used in medicine, especially in the form of a tincture. It is also largely used in the preparation of dyes and organic drugs. Iodoform, a substance used as an antiseptic, has the formula CHI_3.

Hydrogen iodide (HI). This gas can be prepared by passing hydrogen sulfide into water in which iodine is suspended:

$$H_2S + I_2 \longrightarrow 2\,HI + S$$

The resulting hydrogen iodide dissolves in the water, forming *hydriodic acid*, while the sulfur is precipitated.

Properties and uses. Hydrogen iodide resembles the corresponding compounds of chlorine and bromine, but is even less stable. It readily decomposes into hydrogen and iodine, and is therefore *a strong reducing agent.*

The salts of hydriodic acid, the iodides, are, in general, similar to the chlorides and bromides. Potassium iodide is largely used in medicine, and silver iodide in photography.

GAY-LUSSAC'S LAW OF VOLUMES

In the discussion of the composition of hydrochloric acid it was stated that *1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrochloric acid.* With bromine and iodine, similar combining ratios hold good. These facts recall the simple volume relations already noted in the study of the composition of steam (p. 50) and ammonia (p. 127). These relations may be represented graphically in the following way, the squares representing *equal volumes:*

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

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

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

In the early part of the past century the distinguished French chemist, Gay-Lussac (Fig. 23), studied the volume relations of many combining gases, and concluded that similar relations *always* hold. His observations are summed up in the following generalization, known as the law of volumes: *When two gases combine chemically there is always a simple ratio between their volumes, and also between the volume of either one of them and that of the product, provided it is a gas.* By a simple ratio is meant, of course, the ratio of integer numbers, as 1 : 2, or 2 : 3.

EXERCISES

1. How do we account for the fact that liquid hydrofluoric acid is not an electrolyte?

2. Why is hydrogen fluoride obtained by the action of sulfuric acid on fluorite?

3. In the preparation of chlorine, what advantages are there in treating manganese dioxide with a mixture of sodium chloride and sulfuric acid rather than with hydrochloric acid?

4. Why are the methods of preparation used in the laboratory likely to differ from those used commercially?

5. What is the derivation of the word *nascent*?

6. What substances studied are used as bleaching agents? To what is the bleaching action due in each case?

7. What does the term *muriatic acid* signify (see dictionary)?

8. Upon what metals would you expect hydrochloric acid to act? (See Displacement Series.)

9. What is the meaning of the phrase *aqua regia*?

10. A solution of hydriodic acid turns brown on standing. Why?

11. From their behavior toward sulfuric acid, to what class of agents do hydrobromic and hydriodic acids belong?

12. Give the derivation of the names of the elements of the chlorine family.

13. What is formed when a metal dissolves in each of the following: nitric acid; dilute sulfuric acid; concentrated sulfuric acid; hydrochloric acid; aqua regia?

14. In what respects are the elements included in the chlorine family similar?

15. What weight of hydrogen chloride is absorbed by 1 liter of water under standard conditions? *Ans.* 819.9 g. What weight of sodium chloride is necessary to prepare this weight of hydrogen chloride? *Ans.* 1314.34 g.

TOPICS FOR THEMES

Scheele (Thorpe, Essays in Historical Chemistry).

Bleaching (see encyclopedia).

CHAPTER XX

MOLECULAR WEIGHTS; ATOMIC WEIGHTS

Introduction. In Chapter IX it was shown that from the results of a careful analysis of a compound it is easy to calculate a formula, *provided we adopt the simplest one possible.* The method described would lead to the formula HO for hydrogen peroxide, while the formula we have adopted is H_2O_2. The *ratio* of hydrogen to oxygen is the same in these two formulas, and to decide between them we must devise a way to determine the *weight of the molecule* of the compound. If this weight can be shown to be 17.008, the correct formula is HO; if it is 34.016, the formula is H_2O_2. We shall now turn our attention to the problem of determining the molecular weights of compounds.

Avogadro's hypothesis. At the close of the last chapter we saw that two gases always combine in some simple ratio by volume, and that the volume of the product (if it is a gas) is also in simple ratio to that of the other two volumes (law of volumes).

These relations are so simple and so unexpected that we at once feel that they indicate a very simple ratio between the number of molecules present in equal volumes of gases. As early as 1811 the Italian physicist, Avogadro, suggested that the ratios become perfectly intelligible if we assume that *equal volumes of any two gases contain the same number of molecules.* This generalization is known as the *hypothesis of Avogadro*, and it is in complete accord with all we have learned about gases since Avogadro's time.

Avogadro's hypothesis, and molecular weights. Assuming the truth of Avogadro's hypothesis, we have a simple means of deciding upon the *relative* weights of the various kinds of molecules; for if equal volumes of two gases contain the *same number of molecules*, the weights of the two kinds of molecules must be in the same ratio as the weights of the two volumes made up of these molecules.

For example, the weight of a liter of ammonia is 0.7708 g. and that of a liter of hydrogen chloride is 1.6398 g. These two values will therefore indicate the *relative* weights of the two kinds of molecules, since there is the same number of each in a liter. If we adopt some one gas as a standard, we can readily determine the weights of all gaseous molecules relatively to those of the standard gas. Thus, if we adopt ammonia as standard (unity), the molecule of hydrogen chloride is 2.14 times as heavy as the standard.

Oxygen as standard. It will be seen that the gas selected as standard, and the volume chosen for comparison will make no difference, since the weights are all *relative* in any case. But since the molecules are all made up of atoms, it is important that the standard chosen for atomic weights should be in accord with that chosen for molecular weights. For many reasons oxygen serves best for atomic weights, and it is also chosen for molecular weights.

The oxygen atom taken as 16. In Chapter VI we saw that oxygen combines with hydrogen in the ratio 1 : 7.94 by weight. If we wish to take oxygen as a standard for atomic weights, the *smallest* whole number we can assign to it while keeping hydrogen at least unity is 8, hydrogen then becoming 1.008. Adopting these two values, the formula of water will be HO. There is, however, good reason for thinking that there are *two atoms of hydrogen* in a molecule of water. For example, when sodium acts upon water, exactly one half of the hydrogen is given off, and at the same time sodium hydroxide is formed, which contains the other half. This is most simply expressed in the equation

$$H_2O + Na \longrightarrow NaOH + H$$

On the other hand, none of the reactions which water undergoes indicates that there is more than one atom of oxygen in a molecule of water.

If there are *two* atoms of hydrogen and *one* of oxygen in water, then to keep the hydrogen atom at least unity, we must double the value of oxygen, making it 16 instead of 8. The formula of water then becomes H_2O.

The oxygen molecule taken as 32. Since we wish to use oxygen gas as a standard with which to compare other gases, it is important to assign a weight to the oxygen *molecule* that will keep the *atom* equal to 16. Now when hydrogen and oxygen combine to form steam, we have the equation (p. 50):

$$2 \text{ vol. hydrogen} + 1 \text{ vol. oxygen} \longrightarrow 2 \text{ vol. steam}$$

Let us suppose that the 1 volume of oxygen contains 100 molecules; then the 2 volumes of steam must contain 200 molecules (Avogadro's hypothesis). But each of these 200 molecules must contain *at least* one atom of oxygen, or 200 in all, and these 200 atoms came from 100 molecules of oxygen. Therefore each molecule of oxygen must contain at least two atoms of oxygen.

Evidently this reasoning merely shows that there are *at least* two atoms in the oxygen molecule. There may be more than that, but as there is no evidence that this is so, we assume that each oxygen molecule contains only two atoms. If, then, we wish to retain the value 16 for the oxygen *atom*, we must adopt 32 for the value of the oxygen *molecule*.

Molecular weights from weight of 1 liter. We have now devised a method of determining how much heavier one kind of a molecule is than another, and have fixed upon the weight of one standard molecule (oxygen), with which all others can be compared. The determination of molecular weights now becomes easy. For example, 1 liter of oxygen weighs 1.429 g., while 1 liter of hydrogen chloride weighs 1.6398 g. The ratio between the weights of the two kinds of molecules is therefore 1.429 : 1.6398. To compare the hydrogen chloride molecule with oxygen taken as 32, we need only solve the proportion: $1.429 : 1.6398 :: 32 : x$. The molecular weight of hydrogen chloride (x) is therefore 36.7.

Gram-molecular volume equals 22.4 liters. Having adopted 32 as the standard for oxygen, it is of interest to find the volume occupied by the gram-molecular weight of this gas, namely, 32 g. A simple computation from the weight of 1 liter shows this volume to be *22.4 liters*. If we construct a vessel of exactly this content and fill it with oxygen gas, it will contain just enough molecules of oxygen to weigh 32 g., which is our standard weight for oxygen.

If, now, we replace the oxygen by another gas, say, hydrogen chloride, we shall have the same number of molecules present. The weight of hydrogen chloride filling the vessel is 36.45 g. But since there are the same number of molecules, the values 32 and 36.45 must represent the relative weights of the two kinds of molecules. In like manner, the weight of 22.4 liters of *any* gas will give a number which expresses the weight of a molecule of that gas compared with the molecule of oxygen taken as the standard. These relations are illustrated in Fig. 86. We therefore reach the following simple rule: *The molecular weight of any gas may be found by determining the weight in grams of 22.4 liters* *of the gas.* The volume 22.4 liters is called the *gram-molecular volume* of gases. Owing to the fact that most gases do not exactly conform to any of the gas laws, the weight of 22.4 liters of a gas is not its *precise* molecular weight, but is very close to it.

It is evident that this method only applies to elements or compounds that are gases or can be converted into the gaseous state. For all others different methods are known, but their discussion is beyond the scope of an elementary text.

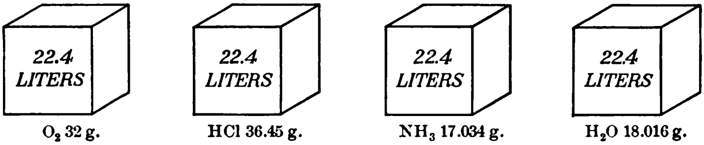


FIG. 86. The weight of 22.4 liters of various gases

Molecular weights of the elements. When we determine the weight of 22.4 liters of the various *elementary* gases, we reach some interesting conclusions. Experiment shows that the molecular weight of many of them, such as nitrogen, hydrogen, chlorine, and bromine give values which are *twice the atomic weights,* so that in these cases the molecule contains two atoms (p. 69). In the case of the metals, so far as their vapors have been studied, the molecular weight and the atomic weight are the same, so that the molecular consists of a single atom. The molecule of ozone contains three atoms of oxygen, so that its formula is O_3; while the molecules of phosphorus and arsenic contain four atoms, giving the formulas P_4 and As_4.

Selection of atomic weights from combining weights. It is now easy to determine which multiple of the combining weight shall be adopted as the correct atomic weight — a problem which we left unsolved in Chapter VIII. (The student should at this point carefully review page 70.) The mode of procedure will be understood most readily by an example; so let us suppose that we have found the combining weight of nitrogen to be 7.005 and that we wish to decide whether this value or some simple multiple, 14.01 or 21.015, is the atomic weight.

We first determine the weight of 22.4 liters of a number of gaseous compounds which we know to contain nitrogen. These values are given in the first column of the table.

NAME OF GASEOUS COMPOUND	MOLECULAR WEIGHT (22.4 LITERS)	PERCENTAGE OF NITROGEN BY EXPERIMENT	PART OF MOLECULAR WEIGHT DUE TO NITROGEN
Nitrogen gas . . .	27.95	100.00	27.95
Nitrous oxide . . .	44.13	63.70	28.11
Nitric oxide . . .	40.00	46.74	14.02
Ammonia	17.05	82.28	14.03
Nitric acid . . .	63.75	22.27	14.30

We next make a careful analysis of each of these compounds to ascertain the percentage of nitrogen present, placing the values obtained in the second column. If we multiply the molecular weight of each compound by the percentage of nitrogen, the product will be the portion of the molecular weight due to nitrogen. But since the molecules are made up of atoms, the part of a molecule due to nitrogen must represent the *sum of the weights of the nitrogen atoms present.* We notice that the numbers in the last column are either very near to 14 or to twice 14 and that none are near 7. If we examine a large number of nitrogen compounds, it is reasonable to expect that we should find some containing only one atom, and since we find none which give a value of less than 14, we assume that this and not 7 or 21 or 28 represents the weight of a nitrogen atom.

Accurate determination of atomic weights. The weight of a given volume of a gas is difficult to determine with great precision, and in consequence the molecular weights of gases as determined by experiment are usually subject to a very considerable error. The portion of nitrogen in 22.4 liters of the various gases is therefore a little uncertain, as will be seen from the values in the last column (above). All these figures tell us is that the true value is *very near* 14. The *combining weight* can be very accurately determined by the analysis of any of these compounds, and is found to be 7.005. It is therefore evident that the accurate atomic weight is twice this value, namely, 14.01.

Summary. These, then, are the steps which must be taken to establish the atomic weight of an element.

1. Determine the combining weight accurately by analysis.

2. Determine the weight of 22.4 liters of a large number of gaseous compounds of the element, and, by analysis, the part of the molecular weights due to the element. The smallest number so obtained will be the *approximate* atomic weight.

3. Multiply the combining weight by the integer (1, 2, or 3) which will give a number close to the approximate atomic weight. The number so obtained will be the *precise* atomic weight.

Equations and volumes of gases. If we have an equation which expresses a reaction in which gaseous molecules take part, we may make use of Avogadro's hypothesis to predict the volume changes which will accompany the reaction. For example, the equation

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

states that 1 gram-molecular weight of hydrogen combines with 1 gram-molecular weight of chlorine to give 2 gram-molecular weights of hydrogen chloride. Now all of these substances are gases, and a gram-molecular weight of every gas occupies the same volume, namely, 22.4 liters. Consequently, 1 volume of hydrogen will combine with 1 volume of chlorine to give 2 volumes of hydrogen chloride, and there will be no change in the volume due to the reaction (save as occasioned by the heat given off). *The coefficients of the molecules therefore indicate the proportion by volume in which gases take part in reactions.*

Weight of a liter of a gas. We have found that a gram-molecular weight of any gas occupies 22.4 liters. If we know the molecular weight of a gas, we can at once deduce the weight of a liter of the gas. For example, the molecular weight of acetylene (C_2H_2) is 26.016. This means that 26.016 g. occupy 22.4 liters. Consequently 1 liter will weigh $26.016 \div 22.4 = 1.1614$ g. In general, to find the weight of a liter of any gas, divide its molecular weight by 22.4. The value so obtained will be close enough to the experimental value for all practical purposes.

EXERCISES

1. What are the relative weights of the molecules of hydrogen and hydrogen chloride, as deduced from a weight of 1 liter of each of these gases? *Ans.* As 1 is to 18.34.

2. Natural gas is largely composed of marsh gas (CH_4). When this burns, the equation for the reaction is as follows:

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

In burning 100 cu. ft. of this gas, what volume of oxygen is consumed? *Ans.* 200 cu. ft. What is the volume of the carbon dioxide formed? *Ans.* 100 cu. ft.

3. Why write $2\,O_2$ rather than $4\,O$ in problem 2?

4. The molecular weight of nitric oxide is 30.01. What is the approximate weight of 1 liter of the gas? *Ans.* 1.34 g.

5. A compound was found to have the composition $H = 5.91\%$, $S = 94.08\%$; mol. wt. = 34.1. Calculate its formula. *Ans.* H_2S.

CHAPTER XXI

CARBON AND SOME OF ITS SIMPLER COMPOUNDS

Occurrence. In the uncombined state carbon is found in nature in several forms. The diamond is practically pure carbon, while graphite and the various forms of coal all contain more or less free carbon. The element also occurs abundantly in the form of compounds. Carbon dioxide is its most familiar gaseous compound. Natural gas and petroleum are largely compounds of carbon and hydrogen. The carbonates, especially calcium carbonate (limestone), constitute great strata of rocks, and are found in almost every locality. All living organisms, both plant and animal (p. 89), contain a large percentage of this element, and the number of its compounds which go to make up the vast variety of animate nature is almost limitless. In the free state carbon occurs in both the crystalline and the amorphous form.

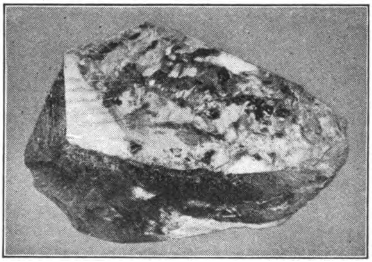


FIG. 87. The Cullinan diamond in its original condition (one half natural size)

Crystalline carbon. Crystalline carbon occurs in two forms — the diamond and graphite.

1. ***Diamond.*** Diamonds are found in certain localities in South Africa, the East Indies, and Brazil. The crystals as

found are usually covered with a rough coating. These are cut so as to bring out the brilliancy of the gem. Diamond cutting is carried on most extensively in Holland.

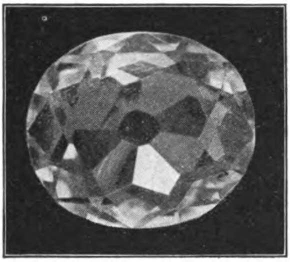


FIG. 88. The Kohinoor diamond after being cut (natural size)

Fig. 87 is a photograph (one half natural size) of the largest diamond ever found, in its original condition. It is known as the Cullinan diamond, and was presented to King Edward VII by the Transvaal government. Fig. 88 is a photograph (natural size) of another very famous diamond (the Kohinoor), in finished form.

The density of the diamond is 3.5, and, though brittle, it is one of the hardest of substances. Few chemical reagents have any action on it, but when heated in oxygen or the air, it blackens and burns, forming carbon dioxide.

Artificial preparation of diamonds. Many attempts have been made to produce diamonds artificially. For a long time these ended in failure, graphite and not diamonds being the product obtained, but in 1893 the French chemist, Moissan (Fig. 77), in his study of chemistry at high temperatures, finally succeeded in making some small ones. He accomplished this by dissolving carbon in melted iron and plunging the crucible containing the mixture into water, as shown in Fig. 89. Under these conditions the carbon crystallized in the iron in the form of the diamond. The diamonds were then freed from the metal by dissolving away the iron in hydrochloric acid.

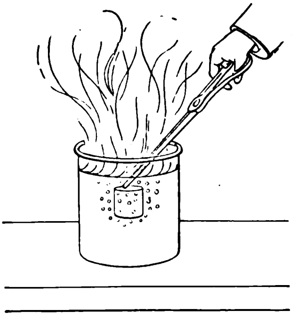


FIG. 89. The artificial preparation of the diamond

[illegible] = [illegible]

2. ***Graphite.*** This form of carbon is found in large quantities, especially in Ceylon, Siberia, and in some parts of the United States and Canada. Large quantities are also made commercially by heating hard coal to a high temperature. It is a glistening black substance, very soft, and greasy to the touch. Its density is about 2.15. It is used in the manufacture of lead pencils and crucibles, as a lubricant, and, in the form of a polish or a paint, as a protective covering for iron.

Commercial production of graphite. The process consists in heating hard coal in large electric furnaces about 40 ft. in length, a longitudinal section of one of which is shown in Fig. 90.

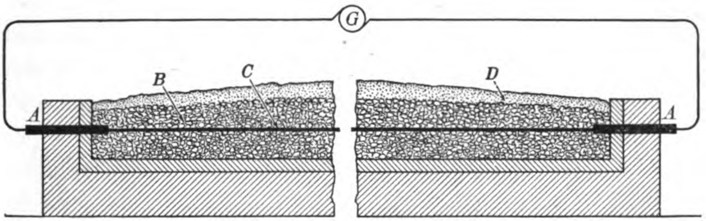


FIG. 90. Electric furnace for the production of graphite

The electrodes *A* are made of graphite. The furnace is nearly filled with the coarse grains of coal *B*. Since the coal is a poor conductor, there is placed in the center of the charge a core *C* of carbon, which serves to conduct the current through the charge. The charge is covered with a mixture, *D*, of sand and carbon (or similar materials), which serves to exclude the air. An alternating current is supplied by the generator *G*. Under the influence of the intense heat produced by the current, the carbon is changed into graphite. Prepared in this way, the product is uniform in composition and free from grit, and is therefore superior to the natural product.

Amorphous carbon. Pure amorphous carbon is best prepared by heating sugar ($C_{12}H_{22}O_{11}$) in the absence of air. The hydrogen and oxygen present are expelled, largely in the form of water, and pure carbon remains. Among the numerous substances that contain amorphous carbon, the following may be mentioned:

1. ***Coal and coke.*** The various forms of coal were formed from vast accumulations of vegetable matter. In hard coal, or anthracite, nearly all the carbon present is in the uncombined state; while in soft, or bituminous coal, a considerable portion of the carbon present is combined with hydrogen, oxygen, nitrogen, and sulfur. When soft coal is heated in the absence of air (see coal gas, p. 210), complex changes occur, resulting in the formation of various useful compounds of carbon, which are given off in the form of gases and vapors, while the mineral matter and free carbon remain and constitute ordinary *coke*. The matter which escapes when coal is heated in the absence of air is known as *volatile matter*. In hard coal the volatile matter averages from 5 per cent to 8 per cent, while in soft coal it averages from 30 per cent to 35 per cent. When coal is burned, the mineral matter present is left in the form of *ash*.

2. ***Charcoal.*** This is prepared from wood just as coke is prepared from coal. The volatile matter expelled contains many valuable substances, such as wood alcohol and acetic acid, which are obtained commercially in this way. Formerly much of this volatile matter was allowed to escape, but at present an increasing amount of charcoal is prepared in such a way that the volatile matter is condensed and saved, as in the heating of coal. Both charcoal and coke are used as fuels, and they are especially useful in reducing metals from their oxides, as will be noted later.

Modern methods for the production of charcoal. Iron cars are loaded with wood *A*, *A* (Fig. 91) and run into the retort *B*. The retort is then made air-tight and heated slowly for twenty-four hours by the fires *F*, *F*. The volatile products escape through the pipes *C*, *C* and then pass into the condensers *D*, *D*. Here those portions which are liquid at ordinary temperatures, such as wood alcohol and acetic acid, are condensed, while the gaseous products are led back into the furnace and burned. When all the volatile matter has been expelled in this way, the cars containing the charcoal are run into cooling chambers, and their place in the retort is taken by other cars loaded with wood.

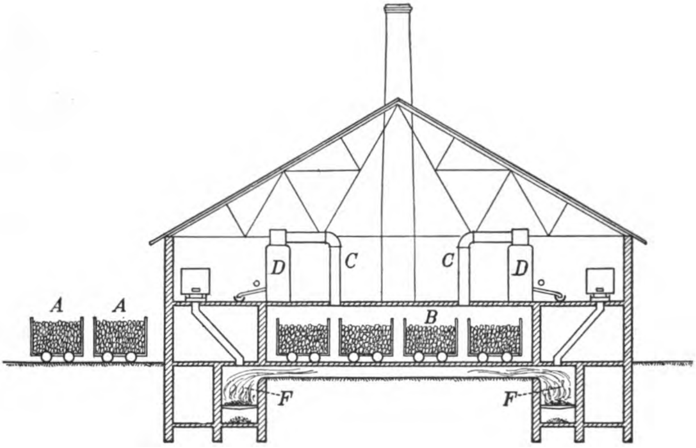


FIG. 91. A modern plant for the production of charcoal

3. ***Bone black, or animal charcoal.*** This is made by charring bones and animal refuse. It consists of very finely divided carbon and of calcium phosphate, and is especially useful for removing coloring matter in the refining of sugar.

4. ***Lampblack.*** Lampblack is a product of the imperfect combustion of carbonaceous fuels, such as oil and gas. It is used in making indelible inks, printer's ink, and black varnishes.

Properties. While the various forms of carbon differ in many properties, especially in hardness, yet they are all odorless, tasteless solids, insoluble in water, and characterized by their stability towards heat. Only in the intense heat of the electric arc does carbon volatilize to any considerable extent.

Chemical conduct. At ordinary temperatures carbon is a very inert substance, but at a higher temperature it combines directly with most of the elements. Because of its strong affinity for oxygen it is an excellent reducing agent. Its compounds with the metals are called *carbides.* One of the most important of these is *calcium carbide* (CaC_2), which is used in the preparation of acetylene. When carbon or a substance containing it, such as wood or coal, burns, the element combines with oxygen to form either carbon dioxide (CO_2) or carbon monoxide (CO). Both of these oxides are colorless gases.

Carbon dioxide; preparation. Attention has already been called (p. 89) to the presence of this gas in the atmosphere and to the various natural processes by means of which it is formed. In the laboratory it is always prepared by the action of an acid upon a carbonate (usually calcium carbonate, in the form of marble). This reaction might be expected to produce carbonic acid, thus:

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2CO_3$$

Carbonic acid is very unstable, however, and decomposes into its anhydride, CO_2, and water, thus:

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

In the preparation of carbon dioxide, pieces of marble are placed in the flask *A* (Fig. 70). Hydrochloric acid is added drop by drop through the funnel tube *B.* The carbon dioxide escapes through *C* and, being heavier than air, collects in the cylinder, as shown in the figure.

Properties. Carbon dioxide is a colorless, almost odorless gas, whose density is 1.5. Its weight may be inferred from the fact that it can be poured like water from one vessel downward into another. At 15° and under ordinary pressure, 1 volume of water dissolves 1 volume of the gas. It is rather easily condensed to a colorless liquid, which is slightly lighter than water and boils at – 78.2°.

Liquid and solid carbon dioxide. The commercial carbon dioxide compressed in steel cylinders is under such great pressure that it is largely in the liquid state. When the pressure is removed, the rapid vaporization of the liquid reduces the temperature sufficiently to freeze a portion of the escaping liquid to a snowlike solid (Fig. 92). Cylinders of liquid carbon dioxide are inexpensive, and should be available in every school. The commercial supply of this gas is obtained largely from fermentation processes, especially from breweries.

To prepare the solid carbon dioxide, the cylinder should be placed across the table and supported in such a way that the stopcock end is several inches lower than the other end. A loose bag is made by holding the corners of a piece of cloth around the neck of the stopcock. The stopcock is then turned on so that the liquid rushes out in large quantities. Very quickly a considerable quantity of the snow collects in the cloth.

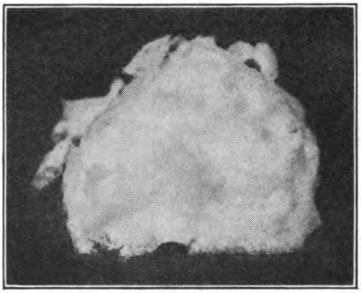


FIG. 92. Carbon dioxide in the solid form

Chemical conduct. Carbon dioxide is neither combustible nor a supporter of combustion. When passed over carbon heated to a high temperature, carbon monoxide is formed:

$$CO_2 + C \longrightarrow 2\,CO$$

Uses. The relation of carbon dioxide to plant life has been discussed in a previous chapter (p. 89). Water highly charged with carbon dioxide is used for making soda water and similar beverages. Ordinary soda water consists of different flavoring extracts, to which is added water highly charged with carbon dioxide. The pressure being removed, the excess of gas escapes, producing *effervescence.* Carbon dioxide is also used as a fire extinguisher. Most of the portable fire extinguishers are simply devices for generating large volumes of the gas. A comparatively small percentage of the gas in air is sufficient to smother a flame.

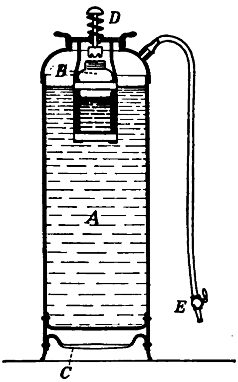


FIG. 93. A portable fire extinguisher

A familiar type of portable fire extinguisher is shown in Fig. 93. The liquid *A* is a solution of sodium carbonate in water. The bottle *B* contains sulfuric acid. In case of fire the apparatus is grasped by the handle *C*, and the knob *D* is pushed in by tapping it against the floor. This breaks the bottle containing the sulfuric acid, which at once reacts with the sodium carbonate, generating carbon dioxide. The pressure of the gas forces the water out through the nozzle *E*. While the volume of water so obtained is not large, it is very effective as a fire extinguisher, because of the carbon dioxide accompanying it.

Carbonic acid (H_2CO_3). This acid is unstable and is known only in the form of a very dilute solution. This solution is most readily prepared by passing carbon dioxide into water:

$$H_2O + CO_2 \rightleftarrows H_2CO_3 \qquad (1)$$

The resulting solution neutralizes bases and, in general, possesses the properties of a weak acid.

The volume of carbon dioxide absorbed in pure water is relatively small. If, however, the water contains a base (such as sodium hydroxide) in solution, the carbonic acid formed according to equation (1) reacts with the base to form the corresponding carbonate:

$$H_2CO_3 + 2\,NaOH \longrightarrow Na_2CO_3 + 2\,H_2O \qquad (2)$$

The removal of the carbonic acid results in the union of more carbon dioxide and water, according to equation (1), so that the absorption of carbon dioxide will continue until the base has been changed into the corresponding carbonate.

Salts of carbonic acid; carbonates. The carbonates form an important class of salts. Limestone, shells, and marble are largely calcium carbonate ($CaCO_3$), common washing soda is sodium carbonate (Na_2CO_3), while baking soda is the acid carbonate ($NaHCO_3$). The carbonates are readily acted upon by acids liberating carbon dioxide (see preparation of carbon dioxide). When heated to a high temperature, most of the carbonates readily decompose, forming carbon dioxide and an oxide of the metal. Thus, *lime* (calcium oxide, CaO) is made by strongly heating calcium carbonate:

$$CaCO_3 \longrightarrow CaO + CO_2$$

Action of carbon dioxide on calcium hydroxide. If carbon dioxide is passed into a solution of calcium hydroxide (ordinary limewater), calcium carbonate is formed and, being insoluble, precipitates:

$$H_2O + CO_2 \longrightarrow H_2CO_3$$
$$Ca(OH)_2 + H_2CO_3 \longrightarrow CaCO_3 + 2\,H_2O$$

Advantage is taken of this reaction in testing for the presence of carbon dioxide. For example, if the air exhaled from the lungs is blown through clear limewater, the solution soon becomes milky, owing to the precipitation of the white solid, calcium carbonate thus proving the presence of carbon dioxide in the exhaled air.

Carbon monoxide. This gas is formed whenever carbon is burned in a limited supply of oxygen:

$$2\,C + O_2 \longrightarrow 2\,CO$$

It is often formed in stoves when the air draft is shut off, especially when hard coal is used as a fuel. Since the gas is very poisonous, care should be taken that the pipes and chimneys are not closed in any way; otherwise the gas may escape into the room and cause the death of those inhaling it.

In the laboratory the gas is usually prepared by heating *formic acid* (H_2CO_2) or *oxalic acid* ($H_2C_2O_4$) with sulfuric acid, which is added to absorb the water formed:

$$H_2CO_2 \longrightarrow H_2O + CO$$
$$H_2C_2O_4 \longrightarrow H_2O + CO_2 + CO$$

Properties and chemical conduct. Carbon monoxide is a colorless gas slightly lighter than air. It is a very treacherous poison, since it is almost odorless.

It is interesting to note that birds are very sensitive to this gas. In mine explosions carbon monoxide is always formed, and rescuers often carry canaries with them, the death of the birds warning the rescuers of their own peril.

Chemically carbon monoxide is quite active. It combines readily with oxygen, and burns in air with a characteristic pale-blue flame (often observed in the combustion of hard coal), forming carbon dioxide

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

It reduces metallic oxides such as copper oxide (CuO), forming the metal and carbon dioxide:

$$CO + CuO \longrightarrow CO_2 + Cu$$

Because of this property carbon monoxide is often used as a reducing agent in liberating the metals from their oxides.

Cyanogen (C_2N_2) and hydrocyanic acid (HNC). At high temperatures carbon unites with nitrogen to form the colorless, very poisonous gas, cyanogen (C_2N_2). With hydrogen and nitrogen it forms *hydrocyanic acid*, often called *prussic acid*. This is a colorless liquid boiling at 26° and is one of the most poisonous substances known. Its vapor is often used to kill insects. The salts of prussic acid are known as *cyanides*. They are likewise very poisonous. Sodium cyanide (NaNC) and potassium cyanide (KNC) are white solids. Their solutions readily dissolve gold, and are used in extracting gold from its ores.

The hydrocarbons. Carbon and hydrogen unite to form a great many compounds. These are known as the *hydrocarbons*. Their importance may be inferred from the fact that, mixed together in varying proportions, they constitute such valuable substances as natural gas, gasoline, kerosene, vaseline, and paraffin.

In order to simplify the study of the hydrocarbons, it is convenient to arrange them in groups, or *series*. The most important of these is the *methane* series. In the following table are given the names, formulas, and boiling points of some of the members of this series having a small number of carbon atoms:

	BOILING POINT		BOILING POINT
Methane (CH_4)	− 160°	Pentane (C_5H_{12})	+ 36°
Ethane (C_2H_6)	− 93°	Hexane (C_6H_{14})	+ 69°
Propane (C_3H_8)	− 45°	Heptane (C_7H_{16})	+ 98°
Butane (C_4H_{10})	+ 1°	General formula (C_nH_{2n+2})	

It will be noted that each member of this series differs from the one preceding it by the group of atoms CH_2, and that the boiling points gradually increase. All the members of this series are known up to the one having the formula

$C_{28}H_{58}$. The lower members are gases, the intermediate members are liquids, and the higher members are solids. They are all combustible.

Petroleum and products derived from it. This liquid is found in the earth in certain localities, the chief oil-producing regions in the United States being Oklahoma, California, Illinois, Texas, and Ohio. By means of compressed air or steam the petroleum is pumped up from deep wells sunk into the ground and is stored in large tanks (Fig. 94). It is composed principally of liquid hydrocarbons in which are dissolved both gaseous and solid hydrocarbons. Crude petroleum is not only used as fuel in this country, particularly on locomotives and steamboats, but many useful products are obtained from it by the process of *refining*, among which are gasoline, kerosene, lubricating oils, vaseline, and paraffin.

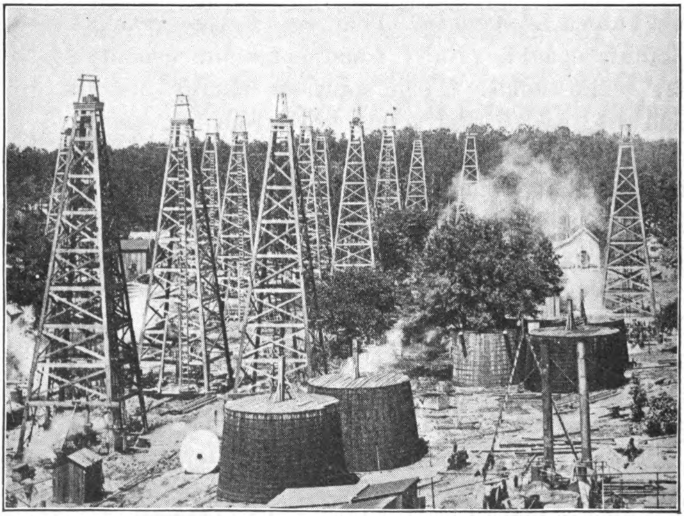


Fig. 94. Oil wells and storage tanks

Refining of petroleum. In this process the crude oil is run into large iron stills (Fig. 95) and subjected to distillation. The distillates which pass over between certain limits of temperature are kept separate and serve for different uses. The liquid passing over between approximately 70° and 150° is known as *naphtha*, while that passing over between 150° and 300° constitutes ordinary *kerosene*. A number of different naphthas are recognized commercially, differing in boiling points and density. Those of low boiling point constitute ordinary *gasoline* and are used as a fuel in stoves and motors; those of higher boiling points are used in making paints. *Benzine* is a high-boiling naphtha, and being a good solvent for such organic substances as fats and oils, is used in cleaning fabrics (dry-cleaning).

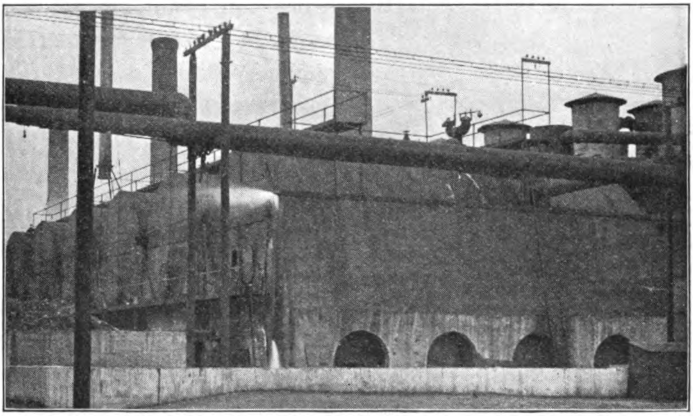


FIG. 95. Stills for refining petroleum

The liquid remaining after the kerosene and higher-boiling oils has distilled over is chilled, whereupon the solid constituents dissolved in the oil separate. These are filtered off, and constitute ordinary *paraffin*. The filtrate is then distilled, and from it various *lubricating oils* are obtained.

Formerly kerosene was the most important of the products obtained from petroleum. At present, however, gasoline is the most in demand, so that every effort is made to increase the yield of gasoline. To accomplish this, the distillation is carried on under conditions that tend to decompose the heavier molecules making up the higher boiling liquids, into the simpler molecules which constitute liquids of lower boiling points. The process is known as the *cracking* of oils.

FIG. 96. Sir Humphry Davy (1778–1829)

A distinguished English scientist, who invented the safety lamp and first prepared the elements sodium and potassium

Methane (CH_4). This hydrocarbon, commonly known as *marsh gas*, is formed in marshes and, in general, wherever organic matter decays or is heated in the absence of air. It constitutes about 30 per cent of coal gas and from 90 per cent to 95 per cent of natural gas. It often collects in mines, and when mixed with air is called *fire damp*. Such mixtures are very explosive.

Pure methane is a colorless, odorless gas about one half as heavy as air. It is but slightly soluble in water. When ignited it burns with a pale-blue flame:

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

Safety lamp. Fortunately the ignition point of fire damp (that is, the temperature at which it takes fire) is high and its flame may be extinguished by cooling. In 1815 Sir Humphry Davy (Fig. 96) invented a miner's lamp based on this principle, in which the usual chimney of a lantern is replaced by a wire gauze (Fig. 97). An explosion flame starting at the wick is so cooled by the metal wire that ignition ceases and the explosion is confined to the interior of the lamp. The principle may be demonstrated by holding a wire gauze a few inches above a Bunsen flame and parallel with the table (Fig. 98). When the gas is turned on and a light applied above the gauze, the resulting flame rests upon the gauze, but does not pass through it to the burner.

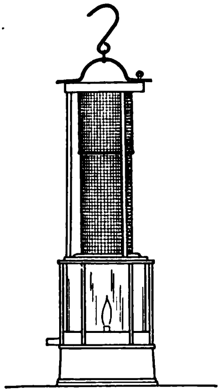


FIG. 97. Miner's safety lamp

Halogen derivatives of methane. As a rule, the hydrogen present in a hydrocarbon may be displaced by a halogen element, atom for atom. In this way there are formed from methane a number of derivatives, the most important of which are the following:

Chloroform ($CHCl_3$), a heavy, colorless liquid boiling at 61°, is the well-known anæsthetic used in surgery. *Carbon tetrachloride* (CCl_4) resembles chloroform in appearance. It is a good solvent, especially for fatty substances. It is often used to remove grease spots from fabrics, and is sold for this purpose under the name of *carbona*. It possesses the advantage over benzine of being noninflammable, but is more expensive. *Iodoform* (CHI_3) is a yellow, crystalline solid and is largely used as an antiseptic in the treatment of wounds.

Acetylene (C_2H_2). This is a colorless gas having, when pure, a faint, pleasant odor. It is easily obtained by the action of water on calcium carbide (CaC_2) (p. 305):

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

In this way the gas is prepared in large quantities for use as an illuminant and as a source of intense heat. When heated it decomposes with evolution of much heat:

$$C_2H_2 \longrightarrow 2\,C + H_2 + 49{,}300 \text{ cal.}$$

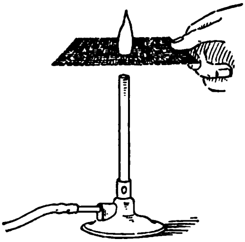


FIG. 98. An experiment illustrating the principle of the safety lamp

When compressed in cylinders, acetylene is very explosive, since the heat liberated in compressing the gas is sufficient to start decomposition. With the proper admixture of air it burns with a brilliant white light. The flame is very hot because to the heat of combustion of the hydrogen and carbon present there is added the heat of decomposition of the acetylene undergoing combustion:

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 603{,}260 \text{ cal.}$$

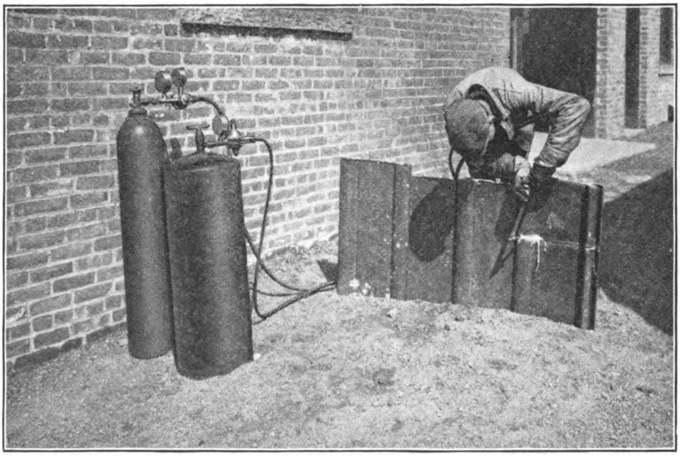


FIG. 99. Cutting an iron plate by means of the oxyacetylene blowpipe

Uses of acetylene. As an illuminant, acetylene is chiefly used when electric lights are not available. It may be safely stored in metal cylinders by filling the cylinder with some porous material (such as asbestos and cotton), partially saturating this with a liquid compound called *acetone*, and then forcing in the gas at low temperatures. Under pressure, the acetone dissolves a large volume of the gas. In this form it is now a common article of commerce.

The intense heat generated by the combustion of acetylene makes it useful in certain processes requiring high temperatures, such as the welding and cutting of metals. For this purpose the acetylene is burned in an apparatus known as the *oxyacetylene blowpipe*, which is very much like the oxyhydrogen blowpipe. A temperature of about 2700° may be obtained in this way. This blowpipe has been found especially useful in cutting iron structures (Fig. 99), since the tip of the flame, when drawn slowly over the metal, melts and burns it at the point of contact, and thus makes it possible to cut the metal into pieces.

EXERCISES

1. Suggest a method for proving that all the various forms of carbon described are really carbon.

2. Suggest a method for determining the percentage of carbon in a sample of coal.

3. How could you distinguish between oxygen, hydrogen, nitrogen, nitrous oxide, and carbon dioxide?

4. Why cannot coal oil be substituted for gasoline in a gasoline engine?

5. Why not burn gasoline in lamps?

6. Calculate the volumes of oxygen necessary to burn 100 liters each of methane, acetylene, and carbon monoxide. *Ans.* 200; 250; 50.

7. Suppose that gasoline is pure heptane, what weight of oxygen would be necessary to burn 1 kg. of the liquid? *Ans.* 3515.5 g.

TOPICS FOR THEMES

(1) Diamond mines. (2) The famous diamonds. (3) Synthetic diamonds. (For information on diamonds, refer to McPherson and Henderson, A Course in General Chemistry; Bird, Modern Science Reader; Duncan, Chemistry of Commerce; and encyclopedia.)

Coal mines and mining (see encyclopedia).

The production and refining of petroleum (Rogers and Aubert, Industrial Chemistry).

CHAPTER XXII

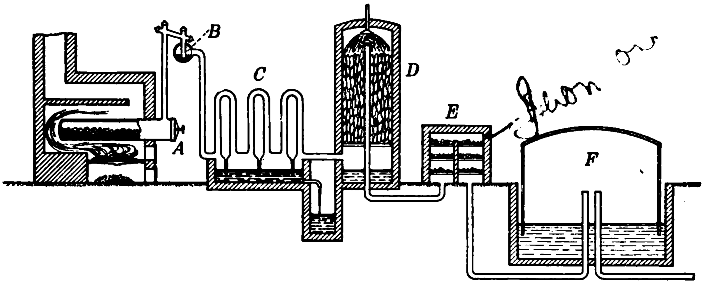
FUELS; FLAMES; ELECTRIC FURNACES

Fuels. A variety of substances are used as sources of heat, the most important of them being the various fuel gases, together with coal, wood, and petroleum. The composition of a number of these fuel gases is given in the table on page 213. Most of them serve as illuminants as well as fuels.

Coal gas. It has been known for several centuries that when soft, or bituminous, coal is heated out of contact with air, combustible gases are formed; indeed, gas obtained in this way was used for street lighting in London and Paris a hundred years ago.

The manufacture of coal gas. The manufacture of coal gas is represented in a diagrammatic way in Fig. 100. The coal is introduced into a closed retort A, and heated by the fire below. A number of these retorts are placed in parallel rows, each being furnished with a delivery pipe, from which the gas bubbles into the tarry liquids which collect in the hydraulic main B, running above the retorts. In this large pipe are deposited most of the solid and liquid products formed in distillation, constituting the sticky mass known as *coal tar*. On the top of the tar there collects a liquid containing ammonia and known as the *ammoniacal liquor*. The partially purified gas then passes into a series of pipes C, in which it is cooled and further separated from tar. In the scrubber D it passes through a column of loose coke, over which water is sprayed, where it is still further cooled and to some extent purified from soluble gases, such as hydrogen sulfide and ammonia. In the purifier *E* it passes over a bed of lime or of iron oxide, which removes the remainder of the sulfur compounds, and from this it enters the large gas holder *F*, from which it is distributed to consumers.

The great bulk of the carbon remains in the retort as *coke* and as *retort carbon.* The yield of gas, tar, and soluble materials depends upon many factors, such as the composition of the coal, the temperature employed, and the rate of heating. One ton of good gas coal yields approximately 10,000 cu. ft. of gas, 1400 lb. of coke, 120 lb. of tar, and 20 gal. of ammoniacal liquor.



Iron ox

FIG. 100. Plant for the manufacture of coal gas and accompanying products

Not only is the ammonia obtained in the manufacture of the gas of great importance, but the coal tar is the source of many very useful substances, as will be explained later.

Water gas. Water gas is essentially a mixture of carbon monoxide and hydrogen. It is made by passing steam over very hot anthracite coal or coke, when the reaction shown in the following equation takes place:

$$C + H_2O \longrightarrow CO + H_2$$

The process is intermittent. The fuel is burned in a draft of air until it is very hot. The air is then shut off and steam turned on. The temperature gradually falls, and when it reaches about 1000°, the process is again reversed.

Water gas is very effective as a fuel, since both carbon monoxide and hydrogen burn with very hot flames. It has little odor and is very poisonous. Its use is therefore attended with some risk, since leaks in pipes are very likely to escape notice.

Enriched water gas. When required merely for the production of heat, the gas as prepared above is at once ready for use. When made for illuminating purposes, it must be *enriched*; that is, illuminants must be added, since both carbon monoxide and hydrogen burn with a nonluminous flame. This is accomplished by passing it into heaters containing highly heated petroleum oils. The gas takes up the gaseous hydrocarbons formed in the decomposition of the petroleum oils, and these hydrocarbons make it burn with a luminous flame.

Producer gas. This is made by burning coal in a limited supply of air so that the product of combustion is largely carbon monoxide. It is used as a fuel in gas engines and in many industrial operations.

Natural gas. In many regions of the United States, as well as in other countries, natural gas is obtained from wells drilled into a stratum holding the gas. While it is variable in composition, it consists largely of methane, many samples containing as much as 95 per cent of this compound. It burns with a rather smoky flame of moderate luminosity, but works well with a gas mantle. It has a high heat of combustion, as shown in the following equation:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 213{,}500 \text{ cal.}$$

It is an ideal fuel and is often conducted through pipes for hundreds of miles from the gas fields to cities.

Comparative composition of fuel gases. The following figures are the results of analyses of average samples, but since each kind of fuel gas varies considerably in composition, the values are to be taken as approximate only. The nitrogen and traces of oxygen are derived from the air.

COMPOSITION OF GASES

CONSTITUENT	OHIO NATURAL GAS	COAL GAS	WATER GAS	ENRICHED WATER GAS	PRODUCER GAS
H_2	0.9	41.3	52.88	37.96	10.90
CH_4	89.5	43.6	2.16	7.09	
C_6H_6	9.3			2.01	
C_2H_2 and C_2H_4 . .	0.3	3.9		9.40	0.60
CO	0.4	6.4	36.80	32.25	20.10
CO_2	0.3	2.0	3.47	4.73	8.50
N_2	0.2	1.2	4.69	3.96	59.90
O_2	0.0	0.3		0.60	
Other hydrocarbons .	0.0	1.5		1.80	

Gas mantles. In using the fuel gases as illuminants, the gas is generally mixed with air before burning. In this way the gas burns with a hot but nearly nonluminous flame. The light is obtained by suspending about this flame a gauze mantle of suitable material. The best mantles are composed of a mixture of 99 per cent of thorium oxide with 1 per cent of cerium oxide.

The thorium and cerium compounds used in gas mantles are obtained from *monazite sand* (Fig. 101) found principally in North Carolina and Brazil. The process of making a gas mantle consists in knitting a cylindrical cotton fabric, which is then dipped into a solution of the nitrates of thorium and cerium. After drying, the fabric is heated, in which process the yarn is burned, while the nitrates of thorium and cerium are converted into oxides (p. 131) which are left in the form of the original fabric. The resulting mantle is very delicate, and is strengthened for shipping by dipping it into a solution of an appropriate substance and drying.

Products of the combustion of ordinary fuels. Ordinary fuels, such as oil, wood, coal, and fuel gases, are largely made up of carbon and hydrogen or their compounds. The chief products of the combustion of such fuels are carbon dioxide and water. Associated with these are small amounts of other products, such as carbon monoxide and sulfur dioxide, the latter being formed from traces of sulfur compounds in the fuels.

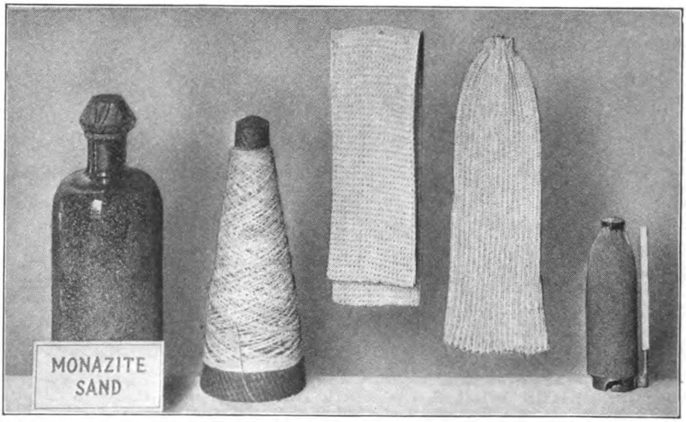


FIG. 101. Materials used in making gas mantles; also different stages in the process

Rooms are not infrequently heated by gas or oil stoves, with no provisions for removing the products of combustion. Likewise, natural gas is often burned in stoves or grates with the damper closed so as to leave no opening into the chimney. Such practices are greatly to be condemned, since the air in the rooms heated in this way soon becomes so contaminated with the various products of combustion as to render it unfit for respiration. The large amount of water vapor formed in rooms so heated condenses on the windows in cold weather, causing the glass to *sweat.*

The electric furnace. In recent years electric furnaces have come into wide use in operations requiring a very high temperature. Temperatures as high as 3500° can easily be reached. These furnaces are constructed on one of two general principles.

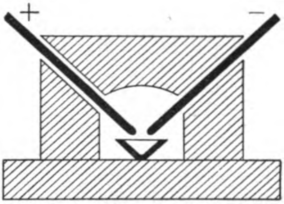


FIG. 102. Electric furnace of the arc type

1. ***Arc furnaces.*** In the one type the source of heat is an electric arc formed between carbon electrodes separated a little from each other, as shown in Fig. 102. The substance to be heated is placed in a vessel, usually a graphite crucible, just below the arc. The electrodes and crucible are surrounded by materials which fuse with great difficulty, such as magnesium oxide, the walls of the furnace being so shaped as to reflect the heat downwards upon the contents of the crucible.

2. ***Resistance furnaces.*** In the other type of furnace the heat is generated by the resistance offered to the current in its passage through the furnace. A typical form of such a furnace is illustrated in Fig. 90, which is used in the manufacture of graphite.

Conditions necessary for flames. When one of the substances undergoing combustion remains solid at the temperature occasioned by the combustion, light may be given off, but there is no flame. Thus, iron wire burning in oxygen throws off a shower of sparks, but no flame is seen. When, however, both of the substances involved are gases or vapors at the temperature reached in the combustion, the act of union is accompanied by a *flame.*

Flames from burning liquids or solids. Many substances which are liquids or solids at ordinary temperatures burn with a flame because the heat of combustion slowly vaporizes them, and the flame is due to the union of this vapor with the oxygen of the air. This may be shown in the case of a candle flame by holding one end of a slender glass tube in the base of the flame (Fig. 103). The unburned vapor in the inner part of the flame is thus conducted away, and may be ignited at the upper end of the tube.

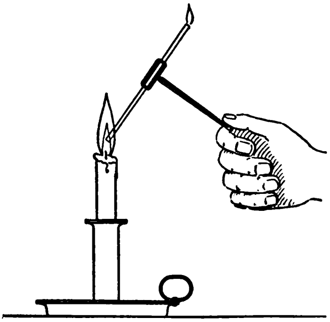


FIG. 103. Method of proving that the interior of a candle flame contains combustible vapors

Structure of a flame. When hydrogen or carbon monoxide burns in oxygen, but one reaction takes place, and as a result the flame is very simple in structure. It consists of a colorless inner cone of unburned gas and an outer cone in which the union between the hydrogen and oxygen is taking place. It follows that the outer cone is the hot part of the flame. That the inner cone is cool is shown by the fact that a match head suspended in this region (Fig. 104) before lighting the gas, and left there while the gas burns, is not ignited.

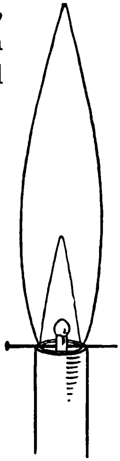


FIG. 104. A match head suspended in lower part of gas flame is not ignited

The flames produced by the combustion of hydrocarbons such as are present in coal gas and natural gas or of mixtures of hydrocarbons with stearic acid, as in candles, is much more complex because several consecutive reactions take place.

For example, in the candle flame (Fig. 105) there are, broadly speaking, three cones: (1) the inner cone *A*, composed of combustible vapors; (2) an intermediate cone *B*, in which these vapors are decomposed by the heat and a small quantity of carbon is set free which renders the flame luminous; and (3) an almost invisible, narrow outer cone, or film, *C*, in which the carbon and hydrogen are burned to water and carbon dioxide.

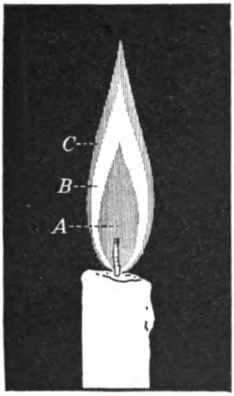


FIG. 105. The cones of a candle flame

Bunsen burners. In the ordinary Bunsen burner, and in similar burners used in gas ranges (Fig. 106) and for illumination with the aid of mantles, the gas is mixed with a certain percentage of air before it is burned. This is accomplished by having an opening (mixer) in the base of the burner (Fig. 106, *A*) into which the air is drawn by the flow of the gas. If the mixer is adjusted so that the proper amount of air is admitted, the flame is colorless. Such a flame possesses an advantage in that it is very hot and no carbon is deposited from it.

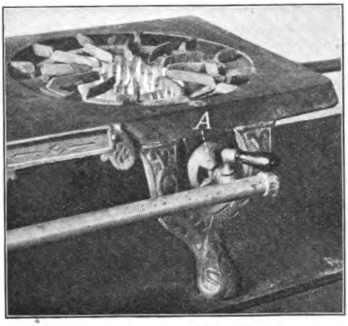


FIG. 106. A typical gas burner

Smoke prevention. Since the products of combustion of fuels are carbon dioxide and water vapor, and these are invisible compounds, it is evident that if the combustion is complete, no smoke will be formed. As a rule the combustion is imperfect; gaseous compounds containing carbon are first formed, and when these are imperfectly burned, a part of their carbon is set free in a finely divided state constituting smoke. Smoke may therefore be prevented by securing the complete combustion of the fuel, the necessary conditions being as follows: (1) a sufficient supply of air; (2) thorough mixing of the air with the combustible gases produced from the fuel; and (3) a temperature high enough to maintain active combustion.

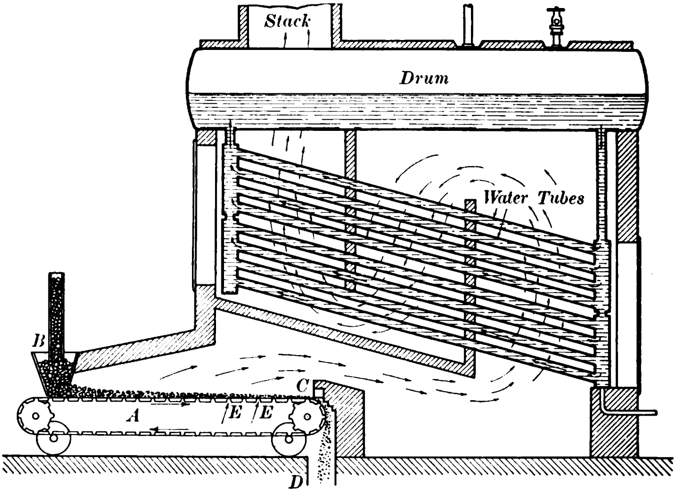


FIG. 107. Diagram of a smoke consumer

Smoke prevention is a problem of great economic importance, especially in the large cities. Thus, for example, it is estimated that the smoke in the city of Pittsburgh costs the people of the city \$10,000,000 yearly, or about \$20 for each inhabitant; and this does not take into account the serious effect of smoke upon health. Because of these facts many cities are now taking steps to abate the smoke nuisance. That the conditions necessary for preventing smoke may be met, it is essential that the coal be introduced into the furnace uniformly, so that the volatile matter expelled upon heating may be more readily mixed with air. This is done efficiently by having a chain grate, as is shown in *A* (Fig. 107). The coal is fed on this at *B*, and as the chain slowly moves forward, the coal gradually enters the furnace, and by the time it reaches the back part of the furnace, *C*, it is completely burned, the ashes falling out at *D*. The volatile matter expelled is thoroughly mixed with hot air led in through the back of the grate *E*, *E*. The large space under the boiler drum gives opportunity for complete combustion of the products under the chimney. The water in the drum circulates through the tubes, as shown by the arrows, and thus is heated to a high temperature.

EXERCISES

1. Why does charcoal usually burn with no flame? How do you account for the flame sometimes observed when it burns?

2. Would anthracite coal be suitable for the manufacture of coal gas?

3. Suggest a way in which natural gas may have been formed.

4. Why does the use of the bellows on the blacksmith's forge cause a more intense heat?

5. Assuming that natural gas is composed wholly of marsh gas, what will be the weight of 1 cu. m. of it (standard conditions)? *Ans.* 716.8 g. What will be the weight of water and of carbon dioxide formed in its combustion? *Ans.* 1611 g.; 1967 g.

6. A portable gas stove used in heating a room burns 10 cu. ft. of gas each hour. Supposing that the gas is pure methane, what volume of oxygen is withdrawn each hour from the air in the room? *Ans.* 20 cu. ft. What volume of carbon dioxide is given off? *Ans.* 10 cu. ft.

TOPICS FOR THEMES

The production and uses of natural gas. (Write to your state geologist for references.)

The use of high temperatures (Duncan, Chemistry of Commerce).

Methods of heating. (Consult local dealers in stoves and furnaces.)

CHAPTER XXIII

CARBOHYDRATES; ALCOHOLS; COAL-TAR COMPOUNDS

Carbohydrates. The term *carbohydrate* is applied to a class of compounds which includes the sugars, starch, and allied substances. These compounds contain carbon, hydrogen, and oxygen, the last two elements usually being present in the proportion in which they combine to form water. The most important carbohydrates are the following:

TABLE OF CARBOHYDRATES

Sucrose (ordinary sugar)	$C_{12}H_{22}O_{11}$
Lactose (milk sugar)	$C_{12}H_{22}$[illegible]$_{11}$
Maltose	$C_{12}H_{22}O_{11}$
Dextrose (grape sugar)	$C_6H_{12}O_6$
Levulose	$C_6H_{12}O_6$
Cellulose	$(C_6H_{10}O_5)_x$
Starch	$(C_6H_{10}O_5)_x$

The molecular formulas of cellulose and starch are unknown but are multiples of the simple formula $C_6H_{10}O_5$; hence they are often written $(C_6H_{10}O_5)_x$. In the discussion of the compounds they will be represented by the simple formula $C_6H_{10}O_5$.

It will be noted that some of the compounds named in the above table have the same formula. Compounds having the same formula are said to be *isomeric.* The difference in the properties of such compounds is due to the fact that the atoms are arranged differently in the molecule.

Sucrose (sugar) ($C_{12}H_{22}O_{11}$). This substance, commonly called *sugar*, occurs in many plants, especially in the sugar cane and sugar beet, each of which at present furnishes about 50 per cent of the total production. The sugar cane grows only in warm climates (Cuba and the Hawaiian Islands are the greatest producers), while the sugar beet thrives in cooler climates, such as prevail in Ohio and Michigan in the United States, and in Germany. The beets contain as high as 16 per cent of sucrose.

The manufacture of sugar. The juice from the cane or beet contains the sugar in solution along with many impurities. These impurities are removed, partly by precipitation and partly by filtering through bone black, and the resulting solution is then evaporated until the sugar crystallizes. The evaporation is conducted in closed vessels from which the air is partially exhausted (vacuum pans (Fig. 108)). In this way the boiling point of the solution is lowered and the charring of the sugar is prevented. It is not practical to remove all the sugar from the solution. Ordinary *molasses* is the solution which remains after the sugar has been crystallized out from the purified juice of the sugar cane. The sweetness of maple sugar is due to sucrose, other products present in the maple sap imparting the distinctive flavor. About 40,000,000,000 lb. of sugar is produced annually. The annual consumption of sugar in the United States amounts to about 8,250,000,000 lb. or approximately 85 lb. for each person.

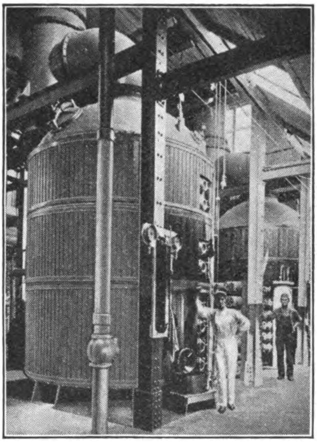


Fig. 108. Vacuum pans in a sugar factory

Chemical conduct of sugar. When a solution of cane sugar is heated to about 70° with hydrochloric acid, two isomeric sugars, *dextrose* and *levulose*, are formed in accordance with the following equation:

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

In this process the sugar is said to be *inverted*, and the mixture of dextrose and levulose is termed *invert sugar*.

When heated to 160°, sucrose melts; if the temperature is increased to about 215°, a partial decomposition takes place, and a brown substance known as *caramel* is formed. This is used extensively as a coloring matter and in making confectionery.

Lactose (milk sugar) ($C_{12}H_{22}O_{11}$). This compound is present in the milk of all mammals. The average composition of cow's milk is as follows:

Water	87.17%
Casein (nitrogenous matter)	3.56%
Butter fat	3.64%
Lactose	4.88%
Mineral matter	0.75%

When *rennin* (a substance obtained from the stomach of calves) is added to milk, the casein separates and is used in the manufacture of *cheese*. The remaining liquid, known as *whey*, contains the milk sugar, which crystallizes on evaporation; it resembles sucrose in appearance, but is not so sweet or so soluble. The souring of milk is due to the fact that the milk sugar contained in it changes into lactic acid, a liquid having the formula $C_3H_6O_3$:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 4\,C_3H_6O_3$$

This change is brought about through the agency of a certain microörganism which enters from the air, and the process is known as *lactic fermentation*. The body of the ordinary medicine tablet consists of lactose, because this substance readily absorbs medicinal solutions.

Dextrose (grape sugar, glucose) ($C_6H_{12}O_6$). This sugar is present in honey and in many fruits, usually associated with levulose, and is often called *grape sugar* because of its presence in grape juice. It can be obtained along with levulose by heating sucrose with hydrochloric acid, as explained above. Commercially it is prepared in enormous quantities by heating starch with hydrochloric acid. The starch is first changed into a sweet-tasting solid known as *dextrin*, and this, on further action, is converted into dextrose:

$$C_6H_{10}O_5 + H_2O \longrightarrow C_6H_{12}O_6$$

When the change is complete, the hydrochloric acid is neutralized by sodium carbonate. Over 50,000,000 bushels of corn are used each year in the United States in the production of dextrose and allied products.

Pure dextrose is a white, crystalline solid resembling sucrose in its properties, but is not so sweet. Most of the dextrose used is in the form known commercially as *glucose*, or *corn sirup*. This is a thick, sirupy liquid and contains, in addition to water, from 30 per cent to 40 per cent dextrose, and from 40 per cent to 50 per cent dextrin. Large quantities of glucose are used in the preparation of jellies, jams, sirups, candy, and other sweets. The federal law requires that when glucose is present in such foods as jellies and jams, the label on the container must state the percentage of glucose present.

Starch ($C_6H_{10}O_5$). This substance is always present in seeds and tubers and is by far the most abundant carbohydrate found in nature. In the United States it is obtained chiefly from corn, about 60 per cent of which is starch. In Europe the potato serves as the principal source.

The manufacture of starch. In manufacturing starch from corn, the corn is first soaked in water containing a little sulfurous acid, to soften the grain. It is then ground coarsely so as not to crush the germ. When the resulting mass is mixed with water, the germ floats, being very light because of the oil which it contains. In this way the germ is separated from the rest of the seed, and from it *corn oil* is prepared. The remaining material, consisting of the starch, the nitrogenous constituent (gluten), and the bran, or outside coating of the grain, is then ground finely, mixed with water, and passed through cloth sieves, which remove the bran. The water containing the starch and gluten in suspension is then allowed to run slowly down long, shallow troughs, the rate of flow being regulated so that the heavier starch sinks to the bottom of the trough while the lighter gluten is washed away. The starch is then removed from the troughs (Fig. 109) and dried. Large quantities of starch are used in making glucose and other foods, for finishing cloth, and for laundry purposes.

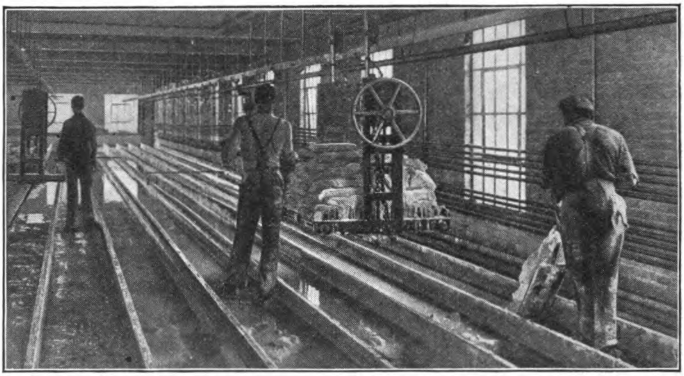


FIG. 109. The interior of a starch factory, showing the settling troughs

Characteristics of starch. Starch consists of minute granules, which differ somewhat in appearance, according to the source of the starch, so that it is often possible from a microscopic examination to determine from what plant any given sample of starch was obtained (Figs. 110 and 111). When heated with water, the granules burst, and the starch partially dissolves. This is the reason why starchy foods are made more digestible by cooking.


FIG. 110. Cornstarch granules magnified 200 diameters

Cellulose ($C_6H_{10}O_5$). This forms the basis of all woody fibers. Cotton and linen are nearly pure cellulose. It is insoluble in water, alcohol, and dilute acids, but will dissolve in a solution prepared by dissolving copper oxide in ammonium hydroxide. Sulfuric acid slowly changes it into dextrose. Concentrated nitric acid forms a mixture of compounds commonly known as *nitrocellulose* or *guncotton.* These are very inflammable and under certain conditions are highly explosive. They have many commercial uses. Photographic films are made from them, as well as from a noninflammable derivative of cellulose known as *acetyl cellulose. Collodion* is a solution of nitrocellulose in a mixture of alcohol and ether. *Celluloid* is a mixture of nitrocellulose and camphor. These two, when mixed together, form a plastic mass which can be molded into any desired shape and which is used for making such objects as combs and brush handles.

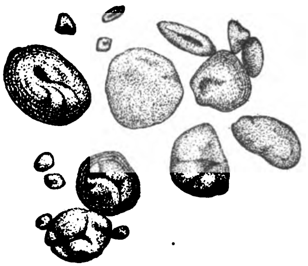


FIG. 111. Wheat-starch granules magnified 200 diameters

Mercerized cotton and artificial silk. When cotton cloth is treated with a concentrated solution of sodium hydroxide, the cellulose shrinks and becomes tougher in character. If the cloth is placed in stretchers to prevent the shrinkage, it assumes an appearance somewhat resembling silk, and is known as *mercerized cotton.* Another fabric prepared in large quantities from cellulose resembles silk very closely, and is known as *artificial silk.* The fiber of this fabric is prepared by forcing concentrated solutions of cellulose or its derivatives through minute tubes and coagulating the cellulose as it emerges in the form of fine threads.

Characteristics of various textile fibers. Of the different fibers used in making the yarns from which the common fabrics are prepared, the vegetable fibers, cotton and linen, are essentially cellulose, while the animal fibers, wool and silk, are composed of nitrogenous substances. Although these fibers resemble each other when viewed with the naked eye, their appearance varies widely when examined with the microscope. The characteristic appearance of these fibers is shown in Fig. 112. It is also possible to distinguish between the fibers by the action of chemical reagents. For example, a hot solution of sodium hydroxide (5 per cent to 10 per cent) has but little action upon cotton, while it will readily dissolve wool and slowly dissolve silk.

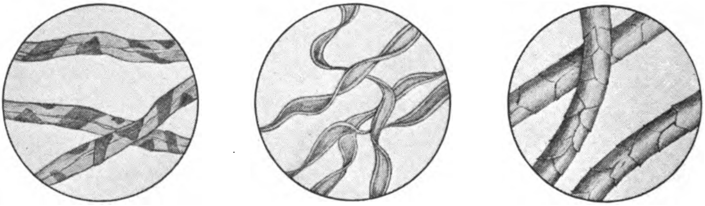

Silk fiber Cotton fiber Wool fiber

FIG. 112. Textile fibers

Paper. Paper consists mainly of cellulose, the finer grades being made from linen and cotton rags and the cheaper grades from wood.

Manufacture of paper. In making paper, the raw material is cut into pieces and treated with suitable reagents (calcium bisulfite is used in case of wood), to remove all objectionable matter, leaving the cellulose, which is then bleached with chlorine. The paper pulp so obtained is suspended in water and run onto wire screens. It then passes between large iron cylinders, some of which are heated with steam. In this way the pulp is pressed and dried and delivered in the form of paper. In the process different materials are often added to the pulp. These vary with the nature of the paper desired; thus, finely ground clay or calcium sulfate is added to give body to the paper. In making paper intended for writing or printing, a compound prepared by heating resin and sodium hydroxide is added, together with aluminium sulfate. This prevents the ink from spreading.

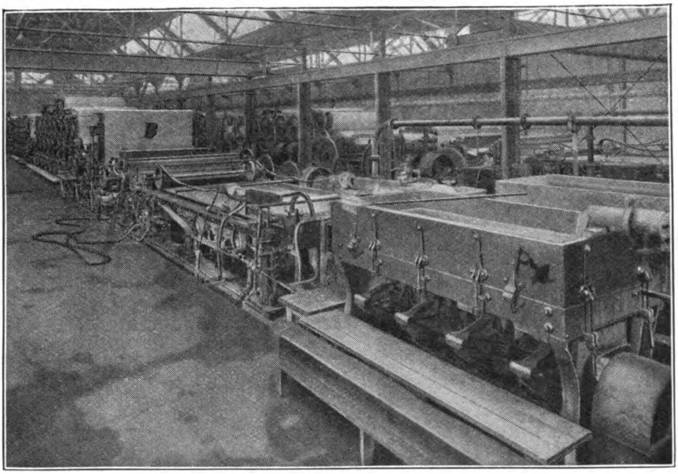


FIG. 113. The interior of a paper mill

Fig. 113 shows the interior of the paper mill. The pulp flows from the container, *A*, onto the screens beyond and then between the rollers until it is pressed and dried and so converted into the finished paper, *B*.

The alcohols. A great many alcohols are known. The two most important ones are methyl alcohol (CH_3OH) and ethyl alcohol (C_2H_5OH).

Methyl alcohol (wood alcohol) (CH_3OH). This compound is formed when wood is heated in the absence of air (p. 196), and on this account it is called *wood alcohol.* It is a colorless liquid which boils at 64.7° and burns with an almost colorless flame. It is a good solvent for organic substances and is used extensively in the manufacture of varnishes. It is quite poisonous. It acts upon the optic nerve, and many persons have become blind from drinking the liquid or from repeatedly inhaling its vapor.

When a mixture of the vapor of methyl alcohol and air is passed over hot copper, the alcohol is oxidized, forming a gaseous compound known as *formaldehyde*:

$$2\,CH_3OH + O_2 \longrightarrow 2\,CH_2O + 2\,H_2O$$

This gas is now prepared in large quantities and used as a disinfectant. A 40 per cent aqueous solution of it is sold under the name of *formalin.*

Ethyl alcohol (grain alcohol, alcohol) (C_2H_5OH). This compound is the one commonly known as alcohol. It resembles methyl alcohol in its general properties.

1. ***Preparation.*** It is prepared by the action of ordinary baker's yeast upon different sugars such as dextrose:

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2$$

This process in which a sugar is changed into alcohol and carbon dioxide by the action of yeast is known as *alcoholic fermentation.* The yeast is a low form of plant life (Fig. 114), and thrives in appropriate sugar solutions. During its growth a number of changes take place which result in converting the sugar into alcohol.

Experimental preparation of alcohol. The formation of alcohol and carbon dioxide from dextrose may be shown as follows: A 10 per cent solution of the sugar in water is poured into flask *A* (Fig. 115) and a little baker's yeast is added. The bottle *B* containing limewater is connected as shown in the figure. The tube *C* is filled with pieces of sodium hydroxide. The temperature is maintained at about 30°. Action soon begins, as is indicated by the rising bubbles of carbon dioxide, and continues for some hours until the sugar is all fermented. That the escaping gas is carbon dioxide is shown by the precipitate formed in *B*. The sodium hydroxide in *C* prevents carbon dioxide from entering from the air. The alcohol formed is separated by distillation.

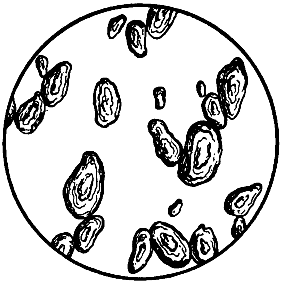


FIG. 114. Some cells of the yeast plant

Commercial preparation of alcohol. Alcohol is prepared commercially from starch obtained from corn or potatoes. The starch is first converted into a sugar known as maltose, by the action of *malt*, a substance prepared by moistening barley with water, allowing it to sprout, and then drying it. This sugar, like dextrose, breaks down into alcohol and carbon dioxide in the presence of yeast. The resulting alcohol is separated by fractional distillation.

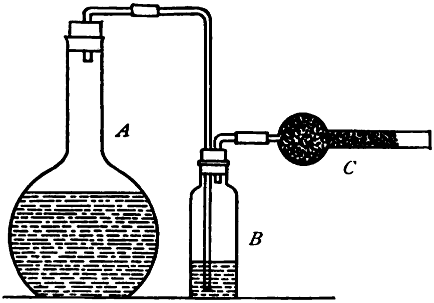


FIG. 115. Laboratory preparation of alcohol

2. ***Properties.*** Ethyl alcohol is a colorless liquid with a pleasant odor, and is an excellent solvent for many organic substances. It boils at 78.3°. It is sometimes used as a

fuel, since its flame is very hot and does not deposit carbon, as the flame from oil does. When taken into the system in small quantities, it causes intoxication; in larger quantities it acts as a poison. The ordinary alcohol of the druggist contains about 95 per cent alcohol and 5 per cent water. A solution containing 99 per cent or more of alcohol is called *absolute alcohol.* When alcohol is heated with sulfuric acid, a low-boiling inflammable liquid known as *ether* is formed:

$$2\,C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2O$$

This is largely used as an anæsthetic in surgical operations.

Denatured alcohol. Ordinary alcohol (95 per cent) sells at about $2.60 per gallon. Of this, $2.10 is a tax imposed by the government. By an act of Congress in 1906 the tax was removed from *denatured alcohol;* that is, alcohol mixed with some substance which renders it unfit for use as a beverage but does not impair its use for manufacturing purposes. The substances ordinarily used for this purpose are methyl alcohol, benzine, and a compound prepared by heating bones and known as pyridine.

Alcoholic liquors. All alcoholic liquors are made by alcoholic fermentation. Wine is made by the fermentation of the dextrose in grape juice and contains from 5 to 15 per cent by volume of alcohol. Beer is made from maltose formed by the action of malt upon starch obtained from various grains, chiefly barley. It contains from 3 to 5 per cent by volume of alcohol. Whisky contains about 50 per cent by volume of alcohol and is made from starch by a process very similar to that described under the commercial preparation of alcohol. Almost any saccharine liquid, such as cider and the juices of fruits in general, undergoes alcoholic fermentation when exposed to air.

Alcoholic liquors, as well as pure alcohol, are taxed by the government. In the year 1912–1913 the revenue collected from this source amounted to over $223,000,000.

Chemical changes in bread-making. The average composition of wheat flour is as follows:

Water	13.8%
Protein (nitrogenous matter)	7.9%
Fats	1.4%
Starch	76.4%
Mineral matter	0.5%

In making bread, flour is mixed with water, yeast, and a little sugar, and the resulting dough is set aside in a warm place for a few hours. The yeast first causes the sugar to undergo alcoholic fermentation. The carbon dioxide formed escapes through the dough, making it light and porous. The yeast plant thrives best at about 30°; hence the necessity for keeping the dough in a warm place. In baking bread the heat expels the alcohol and also expands the bubbles of carbon dioxide caught in the dough, causing it to become porous and making the bread light.

Preservatives. We have observed that the changes taking place in the souring of milk and the changing of sugar into alcohol are caused by low forms of organisms, the cells of which are present in the air. Many other similar changes, such as putrefaction, are due to the same causes. All these changes may be prevented in one of the following ways:

1. By keeping the substance at such a low temperature that the organism causing the change cannot thrive (cold storage).

2. The substance may be heated so as to destroy all organisms present, and then sealed air-tight in a suitable container. This is the method used in canning vegetables and in preserving grape juice and condensed milk.

3. Some substance may be added which in small amounts will destroy the organisms causing the change or will prevent their growth. Such a substance is known as a *preservative.*

Whether or not preservatives should be permitted in foods is a much debated question. Some people maintain that any substance which is powerful enough to prevent the growth of the organisms must have an injurious action upon digestion. The federal government at present allows the use of *sodium benzoate* (a white solid made from a hydrocarbon present in coal tar) in such foods as jellies, jams, and catchup, which are not consumed immediately upon the opening of the container. If this preservative is used, however, the labels on the containers must state the amount present.

Some derivatives of coal tar. In discussing the manufacture of coal gas, it was stated that from the coal tar formed in the process there is obtained a large number of important compounds. These are often spoken of collectively as the *coal-tar compounds.* It is possible here to mention only a few of these.

(1) *Benzene* (C_6H_6) and (2) *toluene* (C_7H_8) are highly inflammable, colorless liquids; (3) *naphthalene* ($C_{10}H_8$) and (4) *anthracene* ($C_{14}H_{10}$) are white, solid hydrocarbons, which are used in the preparation of the two dyes, indigo and alizarin. These dyes were formerly obtained from vegetable sources, but are now manufactured at low cost. Ordinary *moth balls* are nearly pure naphthalene. (5) *Phenol,* or *carbolic acid* (C_6H_5OH), is a white, crystalline solid, very caustic and poisonous. (6) *Cresol* (C_7H_7OH) is a good disinfectant, and is the basis of most of the common disinfectants and sheep dips now on the market.

Each of the above compounds serves as the starting material from which many other useful compounds are prepared. Thus, benzene when treated with nitric acid gives *nitrobenzene* ($C_6H_5NO_2$), and this on reduction yields *aniline* ($C_6H_5NH_2$). Aniline is a nearly colorless liquid, and from it are prepared a large number of dyes of all shades and colors, known as the *aniline dyes.* Toluene when oxidized forms *benzoic acid,* the sodium salt of which (*sodium benzoate*) is used as a food preservative. When phenol is heated with formaldehyde there are obtained products known commercially as *bakelite* and *condensite.* These are useful materials for making buttons, umbrella handles, pipestems, and insulators in electrical apparatus.

Coal-tar compounds in foods. Much discussion has arisen in regard to the use of coal-tar compounds in foods. The federal government has selected seven different aniline dyes of different colors the use of which is permitted in such foods as candies and butter. As already stated (p. 232), the use of *sodium benzoate* as a preservative is allowed under certain restrictions. *Saccharine*, a white solid prepared from toluene and 500 times as sweet as sugar, was formerly permitted in foods, but in 1912 the government forbade the further use of it. *Vanillin*, identical with the compound prepared from vanilla beans, and *coumarin*, which has an odor similar to vanillin, are both used, in artificial vanilla extracts, but when they are so used, the label on the container must state the fact. It is well to keep in mind that all such substances are not foods and are used for purposes other than nutrition.

EXERCISES

1. What is the meaning of the term *carbohydrate* (see dictionary)?

2. Can you tell the difference between pure sugar obtained from sugar cane and that obtained from the sugar beet?

3. It is often said that milk sours readily during thunder showers. What would you say as to the truth of this statement?

4. Why do we use corn rather than dextrose in making alcohol?

5. In separating alcohol from water by distillation, which distills over first?

6. Why does the government permit the use of a preservative (sodium benzoate) in catchup but not in milk?

7. What weight of starch is necessary in making 1 ton of pure dextrose? *Ans.* 1799.93 lb.

8. How could you tell the difference between methyl and ethyl alcohols?

9. Yeast is often added in preparing household beverages. Why is it added? What substance will be present in the beverage so prepared?

10. Why is sugar (or molasses) added in making bread?

11. Alcohol and gasoline boil at about the same temperature and both are combustible. Why not use alcohol as a fuel in place of gasoline?

12. Can you suggest a method for obtaining alcohol from wood?

TOPICS FOR THEMES

Glucose (Lassar-Cohn, Chemistry in Daily Life).

The refining of sugar (Wiley, Foods and their Adulteration).

Alcohol in the industries (Duncan, Chemistry of Commerce).

Uses of cellulose (Duncan, Chemistry of Commerce; Bird, Modern Science Reader).

Paper-making (Rogers and Aubert, Industrial Chemistry; Lassar-Cohn, Chemistry in Daily Life).

CHAPTER XXIV

ORGANIC ACIDS; FATS; OILS; PROTEINS

Organic acids. A great number of acids are known which are composed of carbon, oxygen, and hydrogen, and as a group these are called *organic acids.* Like the hydrocarbons, they can be arranged in series, one of the most important of which is known as the *fatty-acid series.* A few of the most important acids of this series are given in the following table. They are all monobasic — a fact indicated in the formula by separating the replaceable hydrogen atom from the rest of the molecule.

SOME FATTY ACIDS

$H \cdot CHO_2$	formic acid, a liquid boiling at 100°
$H \cdot C_2H_3O_2$	acetic acid, a liquid boiling at 118°
$H \cdot C_4H_7O_2$	butyric acid, a liquid boiling at 163°
$H \cdot C_{16}H_{31}O_2$	palmitic acid, a solid melting at 62°
$H \cdot C_{18}H_{35}O_2$	stearic acid, a solid melting at 69°
$H \cdot C_nH_{2n-1}O_2$	general formula

Of these, acetic acid deserves special mention.

Acetic acid ($H \cdot C_2H_3O_2$). This is the acid which imparts the sour taste to vinegar. It is prepared commercially by the distillation of wood (p. 196). It is a colorless liquid and has a strong, pungent odor. When anhydrous, it crystallizes as a white solid which melts at 18° and closely resembles ice in appearance; hence the name *glacial* acetic acid. Many of the salts of acetic acid are well-known compounds. Thus, lead acetate ($Pb(C_2H_3O_2)_2 \cdot 3\,H_2O$) is the white solid known as *sugar of lead.*

Vinegar. As is well known, when cider is exposed to the air it is gradually transformed into vinegar. Two changes are involved in the process: (1) the sugar in the cider first undergoes alcoholic fermentation, forming *hard cider*, which contains from 4 to 8 per cent of alcohol; (2) the alcohol is then oxidized to acetic acid, the necessary oxygen coming from the air. This oxidation is brought about through the action of the microorganism known as *Mycoderma aceti.* This organism is present in the so-called *mother of vinegar.* The oxidation of alcohol into acetic acid through the agency of the *Mycoderma aceti* is known as *acetic fermentation*, and may be represented as follows:

$$C_2H_5OH + O_2 \longrightarrow H \cdot C_2H_3O_2 + H_2O$$

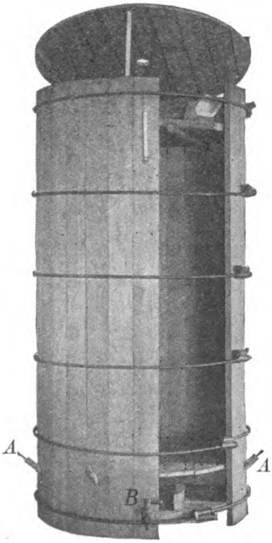


FIG. 116. A vinegar generator

The manufacture of vinegar. The old method of making vinegar consisted simply in storing cider in barrels until the fermentation was complete. In the modern method the change is brought about in a few hours, a large cask, known as a *generator*, being used (Fig. 116). This is filled loosely with beech shavings. Vinegar is first sprayed into the top of the cask in order to introduce the *Mycoderma aceti.* The organism attaches itself to the wood shavings, which are used because they present a large surface. Next a dilute solution of alcohol (hard cider, in the case of cider vinegar) is sprayed into the top of the cask while air is admitted at the bottom *A*, *A*. In this way the alcohol and oxygen are brought into intimate contact, and the oxidation takes place rapidly as the liquid trickles down over the shavings. The resulting vinegar is drawn off at the bottom, *B*, of the cask. Instead of starting with cider, one may use almost any substance which contains starch or sugar, these compounds first being changed into alcohol, as explained in the manufacture of alcohol. In this way are prepared *malt vinegar* from starch and *sugar vinegar* from sugar residues. The cheapest vinegar is made from pure dilute alcohol, and is known as *distilled vinegar*. It is colorless and leaves no residue upon evaporation.

The federal law requires that all vinegar shall contain not less than 4 per cent acetic acid. In addition to the acid, vinegar prepared from fruits and grains contains certain solids derived from the source materials. It is by studying the character of these solids left upon evaporating a sample of vinegar that the chemist is able to determine the source of the vinegar.

Acids belonging to other series. In addition to the fatty acids, the following deserve special mention.

Tartaric acid ($H_2 \cdot C_4H_4O_6$). This is a white solid and occurs in many fruits either in the free state or in the form of its salts. The acid potassium salt ($KHC_4H_4O_6$) occurs in the juice of grapes. When the juice ferments in the manufacture of wine, this salt, being insoluble in alcohol, separates on the sides of the cask and in this form is known as *argol*. When purified, it forms a white solid, which is sold under the name of *cream of tartar* and is used in baking powders (p. 330). The acid itself is often used in soft drinks (pop).

Citric acid ($H_3 \cdot C_6H_5O_7$). This acid occurs in many fruits, especially in lemons. It is a white solid, soluble in water, and is often used as a substitute for lemons in making lemonade.

Oleic acid ($H \cdot C_{18}H_{33}O_2$). The derivatives of this acid constitute the principal part of many oils and liquid fats. The acid itself is an oily liquid.

Fats and oils. The hydrogen of acids can be replaced not only by metals but by *hydrocarbon radicals* as well. The resulting compounds are termed *esters*. The main constituents of the common fats and oils, such as butter, lard, and olive oil, are esters of *oleic*, *palmitic*, and *stearic* acids and are known respectively as *olein*, *palmitin*, and *stearin*. The radical present in these esters is C_3H_5. It is trivalent and is known as the *glyceryl* radical, since it is present in *glycerin* ($C_3H_5(OH)_3$). Since the glyceryl radical is trivalent, and since oleic, palmitic, and stearic acids are all monobasic, it is evident that three molecules of each acid must enter into the formation of each molecule of the ester derived from it. The relation in composition between these acids and the corresponding esters is shown in the following formulas:

$H \cdot C_{18}H_{33}O_2$ (oleic acid)	$C_3H_5(C_{18}H_{33}O_2)_3$ (olein)
$H \cdot C_{16}H_{31}O_2$ (palmitic acid) . . .	$C_3H_5(C_{16}H_{31}O_2)_3$ (palmitin)
$H \cdot C_{18}H_{35}O_2$ (stearic acid)	$C_3H_5(C_{18}H_{35}O_2)_3$ (stearin)

Olein is a liquid and is the main constituent of oils such as olive oil. Palmitin and stearin are white solids. Beef suet is principally stearin.

Butter fat and oleomargarine. While butter fat, like other fats, consists principally of olein, palmitin, and stearin, its characteristic flavor is due to the presence of a small amount (about 8 per cent) of the fat *butyrin*, which is an ester of butyric acid and has the formula $C_3H_5(C_4H_7O_2)_3$. Oleomargarine differs from butter mainly in the fact that a smaller amount of butyrin is present. It is made from the fats obtained from cattle and hogs. Sometimes cottonseed oil is also added. These fats are churned with milk, or mixed with a small amount of butter, in order to furnish sufficient butyrin to give the butter flavor.

In appearance oleomargarine differs from most butter in being nearly colorless. While it is a common practice to color butter artificially, the federal law permits the coloring of oleomargarine only upon the payment of a tax of 10 cents for each pound colored. Many of the states, however, have laws forbidding the sale of oleomargarine that is artificially colored, even though the federal tax has been paid.

Changing oils into solid fats. It will be noted that stearin differs from olein in composition in that it contains 6 atoms of hydrogen more in each molecule. Now if hydrogen is brought in contact with olein under proper conditions and in the presence of a suitable catalytic agent (finely divided nickel is used), the olein takes up the additional hydrogen and is changed into the solid stearin. It is possible in this way to change the oils into solid fats. Certain commercial fats used in cooking, such as that sold under the name of *Crisco*, are made by this process from the comparatively inexpensive cottonseed oil.

The proteins. The term *protein* is applied to a large class of complex nitrogenous compounds which are everywhere abundant in animal and vegetable organisms and which constitute the principal part of the tissues of the living cell. The casein of milk, gluten of flour, and albumin of egg will serve as examples of typical protein matter. The proteins all contain nitrogen, carbon, hydrogen, and oxygen, and some contain sulfur and phosphorus in addition.

EXERCISES

1. Since potassium bitartrate (cream of tartar) is soluble in water, why does it crystallize out when grape juice ferments?

2. How could you prevent cider from changing into vinegar?

3. What is hard cider? How does it differ in composition from sweet cider?

4. Supposing that 95 per cent of the sugar undergoes alcoholic fermentation, what weight of alcohol can be prepared from 100 lb. of dextrose? *Ans.* 48.6 lb. What weight of acetic acid can be prepared from this alcohol? *Ans.* 63.4 lb.

TOPICS FOR THEMES

Catalysis (Duncan, Chemistry of Commerce).

Vinegar-making. (Write to United States Department of Agriculture, Washington, D.C., for bulletins.)

CHAPTER XXV

FOODS

Composition of foods. While the compounds present in our foods are very numerous and often exceedingly complex, yet they may all be included under a few general heads, namely, *proteins*, *fats*, *carbohydrates*, *mineral matter*, and *water*. Since the mineral matter is left as a residue when the food is burned, it is listed as *ash* in reporting the analysis of foods. The composition of the more common foods is given in the table on the opposite page.

Function of foods. Foods have a twofold function

1. They provide the material for the growth of the body as well as for the repair of worn-out tissues.

2. They furnish the necessary energy for muscular work and for maintaining the heat of the body.

Broadly speaking, it may be said that the first of these functions is performed by the protein matter of our foods together with certain mineral salts, while the carbohydrates and fats and, to a certain extent the proteins also, are energy producers. The mineral matter supplies the material for building up the solid tissues of the body, such as the bones, and has in addition more complex functions. Water serves to assist in promoting chemical action and to carry material from one part of the body to another.

While the different classes of food materials are to a certain extent interchangeable, experiments show that a proper mixture of these materials is essential to health. Of course,

AVERAGE COMPOSITION OF EDIBLE PORTION OF TYPICAL FOODS EXPRESSED IN GRAMS PER 100 GRAMS OF FOOD

Food	Water	Protein	Fat	Carbo-hydrate	Ash	Fuel Value (Cal. per 100 g.)
Almonds	4.8	21.0	54.9	17.3	2.0	647
Apples	84.6	0.4	0.5	14.2	0.3	63
Asparagus	94.0	1.8	0.2	3.3	0.7	22
Bacon (smoked)	20.2	9.9	64.8	——	5.1	623
Bananas	75.3	1.3	0.6	22.0	0.8	99
Beans (dried)	12.6	22.5	1.8	59.6	3.5	345
Beans (string)	89.2	2.3	0.3	7.4	0.8	42
Beef (lean steak)	70.0	21.0	7.9	——	1.1	155
Beef (slightly fat)	73.8	22.1	2.9	——	1.2	115
Beets	87.5	1.6	0.1	9.7	1.1	46
Bread (corn)	38.9	7.9	4.7	46.3	2.2	259
Bread (graham)	35.7	8.9	1.8	52.1	1.5	260
Bread (white)	35.3	9.2	1.3	53.1	1.1	260
Butter	11.0	1.0	85.0	——	3.0	769
Cabbage	91.5	1.6	0.3	5.6	1.0	32
Carrots	88.2	1.1	0.4	9.3	1.0	45
Celery	94.5	1.1	0.1	3.3	1.0	19
Chestnuts	45.0	6.2	5.4	42.1	1.3	242
Chicken	63.7	19.3	16.3	——	1.0	224
Codfish (fresh)	82.6	15.8	0.4	——	1.2	67
Corn (green)	75.4	3.1	1.1	19.7	0.7	101
Dates	13.8	1.9	2.5	70.6	1.2	313
Eggs	73.7	14.8	10.5	——	1.0	154
Figs	18.8	4.3	0.3	74.2	2.4	317
Ham (lean, smoked)	53.5	20.2	20.8	——	5.5	268
Lettuce	94.7	1.2	0.3	2.0	0.9	16
Macaroni	78.4	3.0	1.5	15.8	1.3	89
Milk	87.0	3.3	4.0	5.0	0.7	69
Oatmeal	7.3	16.1	7.2	67.5	1.9	400
Olive oil	——	——	100.0	——	——	900
Oranges	86.9	0.8	0.2	11.6	0.5	51
Peaches	89.4	0.7	0.1	9.4	0.4	41
Peanuts	9.2	25.8	38.6	24.4	2.0	548
Peas (green)	74.6	7.0	0.5	16.9	1.0	100
Plums	78.4	1.0	——	20.1	0.5	84
Potatoes	78.3	2.2	0.1	18.4	1.0	83
Prunes (dried)	22.3	2.1	——	73.3	2.3	302
Raisins	14.6	2.6	3.3	76.1	3.4	345
Rice	12.3	8.0	0.3	79.0	0.4	351
Salmon	64.6	21.2	12.8	——	1.4	200
Spinach	92.3	2.1	0.3	3.2	2.1	24
Strawberries	90.4	1.0	0.6	7.4	0.6	39
Tomatoes	94.3	0.9	0.4	3.9	0.5	23
Turnips	89.6	1.3	0.2	8.1	0.8	40
Wheat flour	11.9	13.3	1.5	72.7	0.6	357

These values are taken from *Bulletin No. 28*, office of Experiment Station, Washington, D.C. The fuel values are obtained from the following formula:

Cal. in 100 g. $= 4P + 9F + 4C$, in which P, F, and C represent respectively the number of grams of protein, fat, and carbohydrates in 100 g. of the food (p. 242).

it is true that one can live for many days on a purely protein diet, or on a diet purely of fats and carbohydrates; in fact, persons have been known to live for many days without any food whatever (other than water). In all such cases the body derives the necessary materials from the surplus supply always stored up in the normal body.

The energy value of foods. Experiments show that the heat of the body, as well as the energy used in muscular work, results from the oxidation of food materials. The foods, when eaten, undergo complex changes in which the insoluble portions are converted into soluble compounds. These are absorbed into the system and then either undergo oxidation directly or are temporarily built into tissues which later undergo oxidation. In this process most of the carbon is finally changed into carbon dioxide and exhaled from the lungs, while the hydrogen is changed into water. The nitrogen is excreted largely in the form of urea ($CO(NH_2)_2$).

Broadly speaking, foods may be regarded as fuel from the oxidation of which in the body the energy necessary for the bodily requirements is set free. In the study of foods it is convenient, therefore, to use their *fuel values* (heats of combustion) as a basis of comparison. These values are determined in the calorimeter and expressed in large calories (Cal.), which are 1000 times as large as the small calorie (cal.).

Now experiments show that the body obtains from each of the three classes of foods, when absorbed in the system and oxidized, approximately the following fuel values:

Class of Foods	Calories per Gram	Calories per Pound
Carbohydrates	4	1815
Fats	9	4082
Proteins	4	1815

The amount and nature of foods necessary for health. Many studies have been made in order to find out just how much and what kind of food is best adapted for the preservation of health. Evidently many conditions, such as one's age, weight, and occupation, and the climate in which one lives, enter into the problem.

Since the fats and carbohydrates have nearly the same function, it is sufficient in stating food requirements for a period of, say, twenty-four hours, to give simply the weight of protein necessary, together with the total fuel value. The difference between the total fuel value and that of the required protein gives the number of calories to be supplied from fats and carbohydrates. Such a mixture of these two food materials is selected as will suit the taste, provided only that the fuel value of the mixture together with the fuel value of the protein equals the total fuel value required. The following dietary standards proposed by Atwater are generally accepted. They give the food requirements for a period of twenty-four hours.

Character of Individual	Proteins Required	Fuel Value Required
Man with very hard muscular work (wood-chopper, football player)	175 g.	5500 Cal.
Man with moderately active muscular work	125 g.	3400 Cal.
Man with light to moderate muscular work	112 g.	3050 Cal.
Man at sedentary, or woman with moderately active, work	100 g.	2700 Cal.
Man at rest or woman with light muscular work	90 g.	2450 Cal.
Boy 15 to 16 years	108 g.	3060 Cal.
Boy 13 to 14 years or girl 15 to 16	100 g.	2720 Cal.
Boy 12 to 13 years or girl 14 to 15	87 g.	2380 Cal.
Boy 10 to 11 years or girl 10 to 12	75 g.	2040 Cal.
Boy 6 to 9 years	62 g.	1700 Cal.

The calculation of diets. With the aid of the standards given above and the table giving the composition of foods (p. 241) it is possible to select suitable diets in the case of any individual.

The laws of conservation of energy and matter in the human body. In studying the food requirements of the human body, many experiments have been made to find out whether or not the laws holding good in the inanimate world (namely, the laws of conservation of matter and energy) hold good also in the processes taking place in the living organism. So far as the law of conservation of matter is concerned, the question can be answered by carefully comparing the air breathed and food eaten (*the intake*) with the products stored up in the body and with the products exhaled or excreted (*the output*).

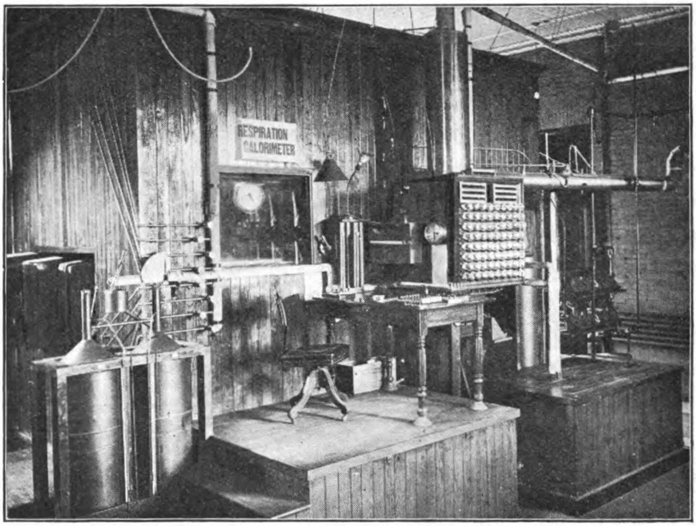


FIG. 117. Exterior of a respiration calorimeter

In order to measure the energy changes, however, one must be able to determine the amount of heat evolved. This is done by means of the *respiration calorimeter.* This is a chamber large enough to enable one to live in it, and constructed with double walls of nonconducting material so as to prevent loss of heat through radiation — in fact, it is a large calorimeter (Fig. 36). Provision is made for introducing air and food.

With the necessary precautions it is possible in this way to measure the heat generated in the body of a person living within the calorimeter. The experiments show that the changes in matter and energy which take place in the human body are in accord with the laws of the conservation of matter and energy.

Fig. 117 shows the exterior of a respiration calorimeter; also the apparatus for analyzing the air admitted, and measuring the heat evolved by the person in the calorimeter.

The cost of food as related to its nutritive value. It will be noted that the food requirements for the body are stated simply in terms of protein, carbohydrates, and fats. It is very evident that the cost of say 100 g. of protein will vary according to the source of the protein. For example, protein obtained in the form of tenderloin steak will cost over 8 times as much as an equal weight of protein obtained from dried beans. Again, there is as much nutriment in 1 lb. of wheat flour (cost, about 4 cents) as in $3\frac{1}{2}$ qt. of oysters (cost, about $1.40). It is interesting that 4 cents' worth of corn meal or oatmeal contains sufficient protein and total fuel value to supply the needs of the body for twenty-four hours. A diet of this kind, however, is not agreeable, since we demand food that is more highly palatable and more attractive to the senses. By finding the selling prices of the various foods given in the table on page 241, one can easily determine the relative cost of various food materials obtained from different sources.

Animal nutrition as contrasted with plant nutrition. Plants build up their tissues from water, nitrogenous matter, and mineral salts absorbed from the soil, and carbon dioxide absorbed from the air. In this process a large amount of energy derived from the sun's rays is absorbed.

Animals, on the other hand, live upon these complex vegetable substances, and in the course of their assimilation the processes which took place in their formation in the plant are largely reversed. The carbon and hydrogen are again liberated, principally as carbon dioxide and water, the nitrogen is secreted largely in the form of urea $CO(NH_2)_2$, while the energy stored up in the plant is utilized as a source of heat and for muscular work. In general, it may be said, therefore, that the processes involved in plant and animal nutrition are opposite in character: *the plant builds up complex tissues out of simple compounds with energy absorption; the animal decomposes these tissues into simple compounds with evolution of energy.*

EXERCISES

1. Is the ash obtained in burning a food present in that form in the food?

2. Why do different nations use different classes of foods?

3. Mention some foods that are rich in water; in protein; in fats; in carbohydrates.

4. Ascertain the current prices of common foods, then work out a list of the most economic ones to use as a source of protein; of carbohydrates; of fats.

TOPICS FOR THEMES

Butter and oleomargarine (Wiley, Foods and their Adulteration).

The cottonseed oil industry (Wiley, Foods and their Adulteration).

CHAPTER XXVI

THE PHOSPHORUS FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT
Phosphorus	P	31.04	1.83	44°
Arsenic	As	74.96	5.73	sublimes
Antimony	Sb	120.2	6.52	630°
Bismuth	Bi	208.	9.80	271°

The family. The elements constituting this family belong in the group with nitrogen, and therefore resemble it in a general way. They exhibit a regular gradation of properties, as is shown in the above table. The same general gradation is also found in their chemical character, phosphorus being an acid-forming element, while bismuth is essentially a metal. The other two elements are intermediate in character.

PHOSPHORUS

History. The element phosphorus was discovered by the alchemist Brandt, of Hamburg, in 1669, while searching for the philosopher's stone (p. 12). Owing to its peculiar properties and the secrecy which was maintained about its preparation, it remained a very rare and costly substance until the demand for it in the manufacture of matches brought about its production on a large scale.

Occurrence. Phosphorus occurs almost entirely in various mineral forms of calcium phosphate. *Phosphorite* is the most abundant of these minerals, while *apatite* consists of calcium phosphate, together with calcium fluoride or chloride. Calcium phosphate is the chief mineral constituent of the bones of animals, and bone ash is therefore nearly pure calcium phosphate.

Preparation. Phosphorus is manufactured from mineral phosphate by heating the phosphate with sand and carbon in an electric furnace. The reaction may be represented in two steps:

$$Ca_3(PO_4)_2 + 3\,SiO_2 \longrightarrow 3\,CaSiO_3 + P_2O_5$$
$$2\,P_2O_5 + 10\,C \longrightarrow 10\,CO + P_4$$

The materials are fed in at *A* (Fig. 118) by the feed screw *B*. The phosphorus vapor escapes at *D* and is condensed under water, while the calcium silicate is tapped off as a liquid at *C*. The phosphorus obtained in this way is quite impure, and is purified by distillation.

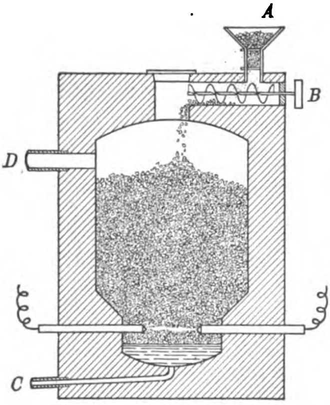


FIG. 118. A furnace for the production of phosphorus

Properties. The purified phosphorus, called *white* or *yellow phosphorus*, is a nearly colorless, translucent, waxy solid which melts at 44° and boils at 287°. It can therefore be cast into any convenient form under warm water, and is usually sold on the market in the form of sticks (Fig. 119). It can be cut with a knife, but this must always be done under water, since phosphorus is extremely inflammable, and the friction of the knife blade is almost sure to set it on fire if cut in the air. It is not soluble in water, but is freely soluble in some other liquids, notably in carbon disulfide. Its density is 1.8.

Chemical conduct. When exposed to the air, phosphorus slowly combines with oxygen, and in so doing gives out a pale light, or *phosphorescence,* which can be seen only in a dark place. The heat of the room may raise the temperature of phosphorus to the kindling point, when it burns with a sputtering flame, giving off dense fumes of oxide of phosphorus. It burns with dazzling brilliancy in oxygen, and combines directly with many other elements. On account of its great attraction for oxygen, it is preserved under water.

Phosphorus is very poisonous, from 0.2 to 0.3 g. being a fatal dose. Ground with flour and grease or similar substances, it is used as a poison for rats and other vermin.

Red phosphorus. On standing, white phosphorus gradually undergoes a remarkable change, being converted into a dark-red powder which has a density varying from 2.1 to 2.38 and is called *red phosphorus.* It no longer takes fire easily, nor is it soluble in carbon disulfide. It is not poisonous and, in fact, is an entirely different substance. The velocity of this change of white phosphorus to red phosphorus increases with rise in temperature, and red phosphorus is therefore prepared by heating the white form a little below the boiling point. When distilled and quickly condensed, the red form changes back to the white.

FIG. 119. Sticks of white phosphorus

Matches. The chief use of phosphorus is in the manufacture of matches, two general varieties of which are in common use. Ordinary friction matches are made by dipping the match sticks first into some inflammable substance, such as melted paraffin, and afterward into a paste consisting of (1) phosphorus sesquisulfide (P_4S_3), (2) some oxidizing substance, such as manganese dioxide or potassium chlorate, and (3) a binding material, usually some kind of glue. The phosphorus sulfide is ignited by friction, the combustion being sustained by the oxidizing agent and communicated to the wood by the burning paraffin. In sulfur matches the paraffin is replaced by sulfur.

In safety matches, a mixture of *red* phosphorus, an oxidizing agent, and some gritty material, such as powdered glass, is placed on the side of the box, while the match tip is provided with an oxidizing agent and an easily oxidizable substance, usually antimony sulfide. The match cannot be ignited easily by friction except on the prepared surface.

Matches were formerly made from white phosphorus, and the workmen frequently suffered from dreadful diseases of the bones of the face. On this account the manufacture and use of matches containing white phosphorus was gradually prohibited in European countries. It was found that the compound P_4S_3, which is easily prepared from white phosphorus, serves just as well, and does not occasion disease, and in 1913 the government of the United States placed a prohibitive tax (two cents per hundred matches) on the white phosphorus match, at the same time forbidding both the import and export of such matches.

Phosphine (PH_3). Phosphine is usually made by heating phosphorus with a solution of potassium hydroxide, the reaction being a complicated one.

A concentrated solution of potassium hydroxide, together with several small bits of phosphorus, is placed in the flask *A* (Fig. 120) and a current of coal gas is passed into the flask through the tube *B* until all the air has been displaced. The gas is then turned off and the flask is heated. Phosphine is formed in small quantities and escapes through the delivery tube, the exit of which is just covered by the water in the vessel *C*. Each bubble of the gas as it escapes into the air takes fire, and the product of combustion (P_2O_5) forms beautiful rings, which float unbroken for a time in quiet air.

Properties. Phosphine is a gas of unpleasant odor and is exceedingly poisonous. Like ammonia, it forms salts with the halogen acids. Thus, we have *phosphonium chloride* (PH_4Cl) analogous to ammonium chloride (NH_4Cl).

Oxides of phosphorus. Phosphorus forms two well-known oxides — the trioxide (P_2O_3) and the pentoxide (P_2O_5) (sometimes called *phosphoric anhydride*). The pentoxide is much the better known of the two. It is a snow-white, voluminous powder whose most marked property is its great attraction for water. It has no chemical action upon most gases, so that they can be very thoroughly dried by being passed through properly arranged vessels containing phosphorus pentoxide.

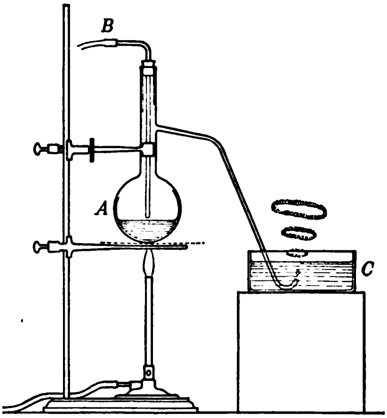


Fig. 120. The preparation of phosphine

Phosphoric acid (H_3PO_4). This acid can be obtained by dissolving phosphorus pentoxide in boiling water, but it is usually made by treating calcium phosphate with concentrated sulfuric acid:

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 \longrightarrow 3\,CaSO_4 + 2\,H_3PO_4$$

The calcium sulfate produced in the reaction is nearly insoluble, and can be filtered off, leaving the phosphoric acid in solution. This acid forms large, colorless crystals which are exceedingly soluble in water. Being a *tribasic* acid, it forms acid as well as normal salts. Thus, the following compounds of sodium are known:

NaH_2PO_4	primary, or monosodium-hydrogen phosphate
Na_2HPO_4	secondary, or disodium-hydrogen phosphate
Na_3PO_4	tertiary, or normal sodium phosphate

They may be prepared by bringing together phosphoric acid and appropriate quantities of sodium hydroxide. Phosphoric acid also forms *mixed salts*; that is, salts containing two different metals. The most familiar compound of this kind is *microcosmic salt*, which has the formula $Na(NH_4)HPO_4$.

Phosphates. The phosphates form an important class of salts. The normal salts are nearly all insoluble, and many of them occur in nature. The secondary phosphates are as a rule insoluble, while most of the primary salts are soluble. The most important phosphate is calcium phosphate, which is mined in enormous quantities for use as a fertilizer (p. 309).

OTHER IMPORTANT COMPOUNDS OF PHOSPHORUS

Phosphorous acid (H_3PO_3): transparent, colorless crystals
Metaphosphoric acid (HPO_3): a white solid, sold in sticks
Pyrophosphoric acid ($H_4P_2O_7$): a white, crystalline solid
Phosphorus trichloride (PCl_3): a colorless, fuming liquid
Phosphorus pentachloride (PCl_5): a white, fuming solid
Phosphorus sesquisulfide (P_4S_3): a solid used in making matches

ARSENIC

Occurrence. Arsenic occurs in nature as the native element, as the sulfides *realgar* (As_2S_2) and *orpiment* (As_2S_3), as the oxide As_2O_3, and as a constituent of many metallic sulfides, of which *arsenopyrite* (FeAsS) is the best known.

Preparation. The element is prepared by heating the arsenopyrite in iron tubes, out of contact with air, when the reaction expressed by the following equation occurs:

$$4\,FeAsS \longrightarrow 4\,FeS + As_4$$

The arsenic, being volatile, condenses in chambers connected with the heated tubes. It is also made from the oxide by reduction with carbon:

$$2\,As_2O_3 + 3\,C \longrightarrow As_4 + 3\,CO_2$$

Properties. Arsenic is a steel-gray solid which resembles coke in appearance and is somewhat brittle. When strongly heated, it *sublimes* (that is, it passes into a vapor without melting), and condenses again to a crystalline solid when the vapor is cooled. About 0.5 per cent of arsenic is added to lead which is to be used for making shot, since it greatly increases the hardness of the lead. Unlike most of its compounds, the element itself is not poisonous, owing to the fact that it is not soluble in the digestive fluids.

Arsine (AsH_3). When any compound containing arsenic is brought into the presence of nascent hydrogen, arsine (AsH_3) is formed. The reaction, when oxide of arsenic is so treated, is represented by the equation

$$As_2O_3 + 12\,[H] = 2\,AsH_3 + 3\,H_2O$$

The symbol [H] indicates that the hydrogen must be in the nascent state.

Arsine is a gas with a peculiar, garliclike odor, and is intensely poisonous. It is an unstable compound, decomposing into its elements when heated to a moderate temperature. It is combustible, burning with a pale bluish-white flame to form arsenic trioxide and water when air is in excess:

$$2\,AsH_3 + 3\,O_2 \longrightarrow As_2O_3 + 3\,H_2O$$

When the supply of air is deficient, water and metallic arsenic are the products:

$$4\,AsH_3 + 3\,O_2 \longrightarrow 6\,H_2O + As_4$$

These reactions make the detection of even minute quantities of arsenic a very easy matter.

Marsh's test for arsenic. The method devised by Marsh for detecting arsenic is most frequently used, the apparatus being shown in Fig. 121. Hydrogen is generated in the flask *A* by the action of dilute sulfuric acid on zinc, is dried by being passed over calcium chloride in the tube *B*, and, after passing through the hard-glass tube *C*, is ignited at the jet *D*. If a substance containing arsenic is now introduced into the generator *A*, the arsenic is converted into arsine by the action of the nascent hydrogen, and passes to the jet along with the hydrogen. If the tube *C* is strongly heated at some point near the middle, the arsine is decomposed while passing this point and the arsenic is deposited just beyond the heated point in the form of a shining brownish-black mirror. A small fraction of a milligram of arsenic can be detected by this test.

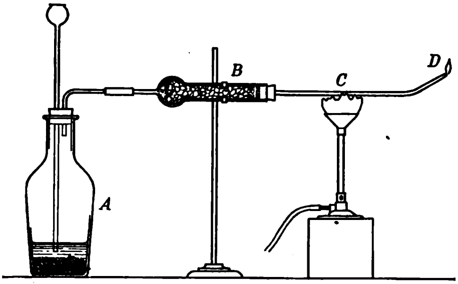


FIG. 121. Marsh's apparatus for the detection of arsenic

Arsenious oxide (white arsenic) (As_2O_3). Arsenious oxide is obtained as a by-product in various metallurgical processes, and in burning pyrite which contains arsenopyrite for the production of sulfur dioxide:

$$2\,FeAsS + 5\,O_2 \longrightarrow Fe_2O_3 + As_2O_3 + 2\,SO_2$$

The arsenious oxide is condensed in appropriate chambers. It is a rather heavy substance, obtained either as a crystalline powder or in lumps resembling porcelain in appearance. It is very poisonous, from 0.2 to 0.3 g. being a fatal dose. Arsenious oxide is used in glass-making and in the dye industry, and as the source from which all other arsenic compounds are made.

Arsenic insecticides. Several compounds of arsenic have important uses as insecticides. *Paris green* and *Scheele's green* are made by treating solutions of copper salts with arsenious oxide. *Lead arsenate* ($Pb_3(AsO_4)_2$) is widely used in connection with lime-sulfur sprays (p. 144).

OTHER COMPOUNDS OF ARSENIC

Arsenious acid (H_3AsO_3): known only in solution

Arsenic acid (H_3AsO_4): colorless transparent crystals

Arsenious sulfide (As_2S_3): a yellow solid, prepared by treating an arsenious compound with hydrogen sulfide

Arsenic sulfide (As_2S_5): a yellow solid, prepared by treating an arsenic compound with hydrogen sulfide

ANTIMONY

Occurrence. Antimony occurs in nature chiefly as the sulfide Sb_2S_3, called *stibnite*, though it is also found as oxide and as a constituent of many complex minerals.

Preparation. Antimony is prepared from the sulfide in a very simple manner. The sulfide is melted with iron in a furnace, when the iron combines with the sulfur to form a liquid layer of melted iron sulfide, while the heavier antimony sinks to the bottom and is drawn off from time to time. The reaction involved is represented by the equation

$$Sb_2S_3 + 3\,Fe \longrightarrow 2\,Sb + 3\,FeS$$

Properties. Antimony is a silvery, metallic substance whose density is 6.52. It is highly crystalline, hard, and very brittle. For a metal it has a rather low melting point (630°), and it expands very noticeably on solidifying. Its chief use is in making Babbitt metal and other alloys (p. 258).

Chemical conduct. In chemical conduct, antimony resembles arsenic in many particulars. It forms the oxides Sb_2O_3 and Sb_2O_5 and the hydride SbH_3 (called *stibine*). It also forms a number of acids. It is, however, much more pronouncedly a metal, dissolving in concentrated sulfuric acid to form the sulfate $Sb_2(SO_4)_3$, and in aqua regia to form the chloride $SbCl_3$. Hydrogen sulfide passed into a solution of the chloride precipitates the orange-colored sulfide Sb_2S_3, having the same composition as the black mineral stibnite.

BISMUTH

Occurrence and preparation. Bismuth is usually found in nature in the uncombined form. It also occurs as oxide and sulfide. Most of the bismuth of commerce comes from Saxony and from Australia and Colorado, but it is not an abundant element. The metal is prepared by merely heating an ore containing the native bismuth, and allowing the melted metal to run out into suitable vessels. Other ores are converted into oxides and reduced by heating with carbon.

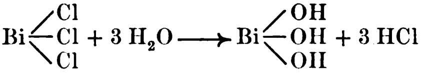
Properties. Bismuth is a heavy, crystalline, brittle metal nearly the color of silver, but with a slightly rosy tint which distinguishes it from other metals. It melts at a low temperature (271°) and has a density of 9.8. It is not acted upon by hydrochloric acid, being below hydrogen in the displacement series (p. 112), but nitric and sulfuric acids act upon it in the same way that they do upon copper.

Compounds of bismuth. Unlike the other elements of this group, bismuth has almost no acid properties. Its chief oxide, Bi_2O_3, is basic in its properties. It dissolves in concentrated acids and forms salts of bismuth:

$$Bi_2O_3 + 6\,HCl = 2\,BiCl_3 + 3\,H_2O$$
$$Bi_2O_3 + 6\,HNO_3 = 2\,Bi(NO_3)_3 + 3\,H_2O$$

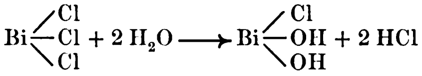
The nitrate and chloride of bismuth can be obtained as well-formed colorless crystals. When treated with water the salts are decomposed in the manner explained in the following paragraph:

Hydrolysis of bismuth salts. The hydroxide $Bi(OH)_3$ is a very weak base, and we should expect its salts to be decomposed, or *hydrolyzed*, by water (p. 138). If bismuth chloride ($BiCl_3$), were to be *completely* hydrolyzed, the equation would be as follows:



$$\mathrm{Bi}\begin{array}{l}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{array} + 3\,H_2O \longrightarrow \mathrm{Bi}\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array} + 3\,HCl$$

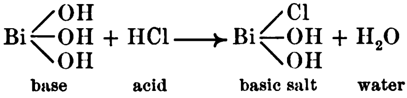
The reaction is not so complete, however — only two of the three chlorine ions being replaced by hydroxyl ions:



$$\mathrm{Bi}\begin{array}{l}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{array} + 2\,H_2O \longrightarrow \mathrm{Bi}\begin{array}{l}\diagup\mathrm{Cl}\\ -\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array} + 2\,HCl$$

If we wish to prevent this hydrolysis, we must add hydrochloric acid in sufficient quantity to reverse the reaction of hydrolysis (p. 136). The compound $Bi(OH)_2Cl$ easily loses water, forming a white solid, BiOCl, known as *bismuthyl chloride.* A similar compound, $BiONO_3$, is known as *bismuth subnitrate*, and is used largely in medicine.

Basic salts. The compound formed by the partial hydrolysis of bismuth chloride is unlike any we have yet met. Since it contains hydroxyl radicals combined with a metal, we must regard it as a *base*; but it also contains a chlorine atom combined with a metal, so that it is likewise a *salt.* Since it has the characteristics of both a base and a salt, it is called a *basic salt. A basic salt may in general be regarded as a base, a part of whose hydroxyl groups have been replaced by an acid:*



$$\underset{\text{base}}{\mathrm{Bi}\begin{cases}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{cases}} + \underset{\text{acid}}{\mathrm{HCl}} \longrightarrow \underset{\text{basic salt}}{\mathrm{Bi}\begin{cases}\mathrm{Cl}\\ \mathrm{OH}\\ \mathrm{OH}\end{cases}} + \underset{\text{water}}{\mathrm{H_2O}}$$

ALLOYS

Some metals when melted together thoroughly intermix, and on cooling form a metallic-appearing substance called an *alloy.* Not all metals will mix in this way, and in some cases definite chemical compounds are formed and separate out as the mixture solidifies, thus destroying the uniform quality of the alloy. In general, the melting point of the alloy is below the average of the melting points of its constituents, and it is usually lower than that of any one of them.

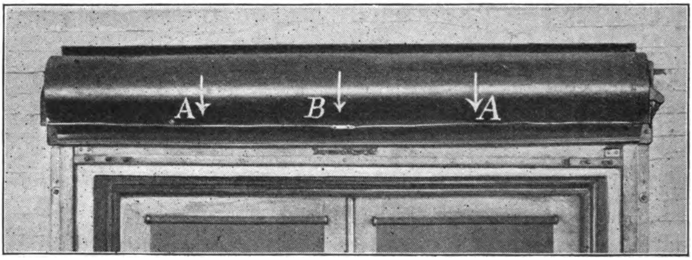


FIG. 122. An automatic fire curtain over a door

Both antimony and bismuth alloy readily with many other metals. The alloys so formed are heavy, are easily melted, do not oxidize easily nor act upon water, and, in general, are well adapted to many technical uses. The manufacture of alloys constitutes the chief use of these two metals.

Antimony imparts to its alloys the property of expanding slightly in solidification, which renders them especially useful in type founding, where fine lines are to be reproduced on a cast. *Type metal* consists of antimony, lead, and tin. *Babbitt* metal, used for journal bearings in machinery, contains the same metals in a different proportion, together with a small percentage of copper.

Bismuth is particularly valuable in the production of very low-melting alloys. For example, *Wood's metal*, consisting of bismuth, lead, tin, and cadmium, melts at 60.5°. The low melting point of such alloys is turned to practical account in making safety plugs in boilers, automatic fire curtains and automatic water sprinklers in buildings, and many similar devices.

Fig. 122 shows a fire curtain, which is held in place by two wires A, A, joined at B by a bismuth alloy. In case of fire, the alloy melts and the wires holding the curtain up are thereby released and the curtain drops, covering the door.

EXERCISES

1. Name all the elements so far studied which may be obtained in different forms.

2. In the preparation of phosphine, why is coal gas passed into the flask? What other gases would serve the same purpose?

3. Could phosphoric acid be substituted for sulfuric acid in the preparation of the common acids?

4. What weight of arsenic can be obtained by heating 500 g. of arsenopyrite? *Ans.* 230.12 g.

5. What was the philosopher's stone?

TOPICS FOR THEMES

The invention of matches (see encyclopedia).

Alloys (see encyclopedia).

CHAPTER XXVII

SILICON AND BORON

SILICON

Occurrence. Next to oxygen, silicon is the most abundant element. It occurs in nature chiefly in the form of SiO_2, called silicon dioxide (*silica*); or in the form of salts of silicic acids (*silicates*). These compounds form a large fraction of the earth's crust, constituting almost all of the common rocks except limestone. Plants absorb small amounts of silica from the soil, and it is also found in minute quantities in animal organisms, especially in hair, claws, and horns.

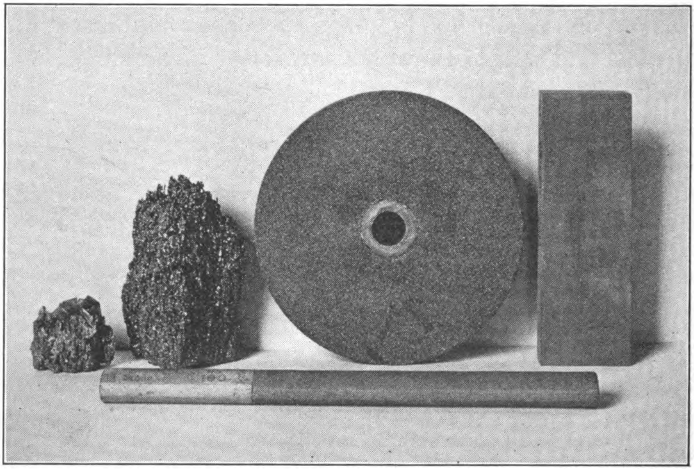


FIG. 123. Carborundum crystals and abrasive objects made of carborundum

The element. Silicon is prepared on the large scale by heating pure sand with carbon in an electric furnace to a very high temperature:

$$SiO_2 + 2\,C \longrightarrow Si + 2\,CO$$

It is a silvery, metallic-appearing substance, highly crystalline and very brittle. It is used in the manufacture of certain varieties of iron.

Silicides. As the name indicates, silicides are compounds consisting of silicon and some one other element. They are very stable at high temperatures, and are usually made by heating the appropriate substances in an electric furnace.

The most important silicide is *carborundum*, which is a silicide of carbon of the formula CSi. It is made by heating coke and sand in an electric furnace, the process being extensively carried on at Niagara Falls. The following equation represents the reaction:

$$SiO_2 + 3\,C \longrightarrow CSi + 2\,CO$$

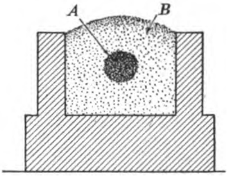


FIG. 124. Cross section of a charged carborundum furnace before heating

The substance so prepared consists of beautiful purplish-black crystals, which are surpassed in hardness only by the diamond and by boron carbide. Carborundum is used as an abrasive; that is, as a material for grinding and polishing very hard substances. Fig. 123 shows two samples of the crystalline material, as well as whetstones and a grinding-wheel prepared from carborundum.

Manufacture of carborundum. The mixture of materials is heated in a large resistance furnace, similar to the one employed in the manufacture of graphite (p. 195). Fig. 124 represents a cross section of the furnace after charging, *A* being the carbon core and *B* the coke and sand. Fig. 125 shows the appearance after heating. *A* is the core of carbon, surrounded by crystallized carborundum *B*. Around this is a shell of amorphous carborundum *C*, while *D* is unchanged charge.

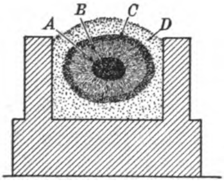


FIG. 125. Cross section of a charged carborundum furnace after heating

Silicon dioxide (silica) (SiO_2). This substance is found in a great variety of forms in nature, both in the amorphous and in the crystalline condition. In the form of *quartz* (Fig. 126) it is found in beautifully formed six-sided prisms, sometimes of great size. When pure it is perfectly transparent and colorless. Some colored varieties are given special names, as amethyst (violet), rose quartz (pale pink), smoky or milky quartz (colored and opaque). Other varieties of silicon dioxide, some of which also contain water, are chalcedony, onyx, jasper, opal, agate, and flint. Sand and sandstone are largely silicon dioxide.

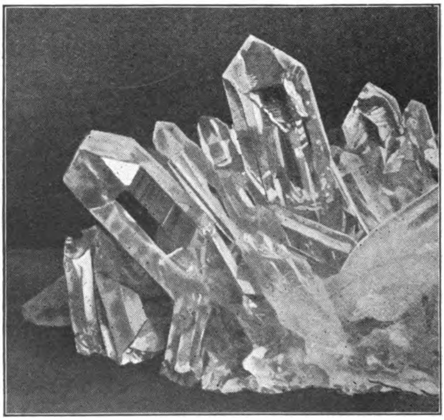


FIG. 126. Quartz crystals

The skeletons of certain microörganisms (infusoria) are composed of nearly pure silica. In some localities these have accumulated in immense deposits, forming a very fine and sharp sand, called *infusorial earth.* This material is often used as a scouring powder, especially in scouring-soaps.

Properties. As obtained by chemical processes, silicon dioxide is an amorphous white powder. In the crystallized state it is very hard, and has a density of 2.6. Pure silica begins to soften at about 1600°, and somewhat above this temperature it can be drawn out into threads and blown into tubes and small vessels like glass. These articles are attacked by comparatively few ordinary reagents, and they do not expand or contract to any appreciable extent with even very great changes in temperature. On this account a quartz vessel can be heated red hot and plunged into cold water without cracking. Fig. 127 shows a quartz crucible and quartz tubes on a wire triangle used to support the crucible when heated.

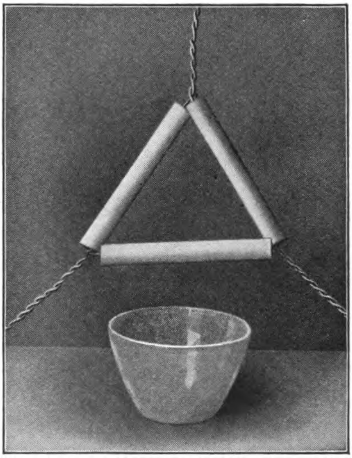


FIG. 127. A crucible and a triangle made from quartz

Chemical conduct. Silica is insoluble in water and in most acids. It is very stable, so that the oxygen which it contains can be removed only by the most powerful reducing agents, and at very high temperatures. Hydrofluoric acid attacks it readily (p. 168), according to the equation

$$SiO_2 + 2\,H_2F_2 \longrightarrow SiF_4 + 2\,H_2O$$

Since it is the anhydride of an acid, it dissolves in fused alkalies to form *silicates.* Being nonvolatile, it will drive out most other anhydrides when heated to a high temperature with their salts, especially when the silicates so formed are fusible. The following equations illustrate this property:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$
$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3$$

Silicic acids. Silicon forms two simple acids, *orthosilicic acid* (H_4SiO_4) and *metasilicic acid* (H_2SiO_3). Orthosilicic acid is formed as a jellylike mass (colloid) when orthosilicates are treated with strong acids. If one attempts to dry this acid, it loses water, passing into metasilicic acid (common silicic acid):

$$H_4SiO_4 \longrightarrow H_2SiO_3 + H_2O$$

Metasilicic acid, when heated, breaks up into silica and water, thus:

$$H_2SiO_3 \longrightarrow H_2O + SiO_2$$

Salts of silicic acids; silicates. A number of salts of the orthosilicic and metasilicic acids occur in nature. Thus, *mica* ($KAlSiO_4$) is a mixed salt of orthosilicic acid.

Polysilicic acids. Silicon has the power to form a great many complex acids which may be regarded as derived from the union of several molecules of orthosilicic acid, with the loss of water. These are called *polysilicic acids.* For example, we have

$$3\,H_4SiO_4 \longrightarrow H_4Si_3O_8 + 4\,H_2O$$

Salts of these acids make up the great bulk of the earth's crust. *Feldspar,* for example, has the formula $KAlSi_3O_8$, and is a mixed salt of the acid $H_4Si_3O_8$, whose formation is represented in the equation above. *Kaolin,* or pure clay, has the formula $H_4Al_2Si_2O_9$, or as commonly written, $Al_2Si_2O_7 \cdot 2\,H_2O$. *Granite* is composed of crystals of feldspar and mica, cemented together with amorphous silica.

Water glass. A concentrated solution of sodium silicate (Na_2SiO_3) or of potassium silicate (K_2SiO_3) or of both is called *water glass.* It is a thick, sticky liquid made by fusing sand with the carbonate of sodium or of potassium. It is used for the purpose of giving a glazed waterproof surface to porous materials, such as wood, stone, and plaster; to render curtains noninflammable; as a glue for glass and pottery; and as an ingredient in cheap soaps.

Its property of closing pores is turned to account in preserving eggs for winter use. The eggs are packed in crocks and then covered with a liquid made by adding 1 volume of commercial water glass to 10 volumes of water. Over the liquid is then poured a little melted paraffin, which soon hardens and excludes the air. Fresh eggs can easily be preserved for from eight to ten months in this way.

Glass. When sodium silicate, calcium silicate, and silicon dioxide are heated together to a very high temperature, the mixture slowly fuses to a transparent liquid, which, on cooling, passes into the rigid material called *glass.* Instead of starting with the silicates of sodium and calcium, it is more convenient and economical to heat sodium carbonate (or sulfate) and lime with an excess of clean sand, the silicates being formed during the heating:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$
$$CaO + SiO_2 \longrightarrow CaSiO_3$$

Molding and blowing glass. The way in which the melted mixture is handled in the glass factory depends upon the character of the object to be made. Many articles, such as bottles, are made by blowing the plastic glass into hollow molds of the desired shape. The mold is opened, a lump of plastic glass on a hollow rod is lowered into it, and the mold is then closed. By blowing into the tube the glass is forced into the shape of the mold. The mold is then opened (Fig. 128) and the object lifted out. The top of the object must be cut off at the proper place and the sharp edges rounded off in a flame. Bottles are now more often made by machinery, in which process the neck is finished first and the bottle then blown by compressed air.

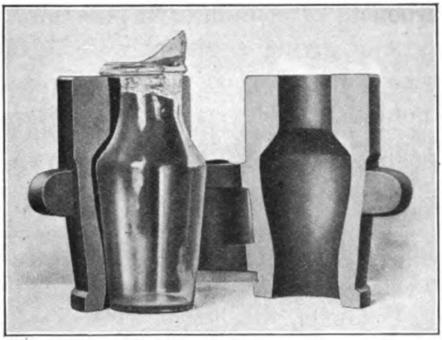


Fig. 128. Making a glass object in a mold

Other objects, such as lamp chimneys, glasses, and beakers, are revolved while being blown in the mold, and have no ridge showing where the mold closes. Window glass is made by gathering a lump of molten glass on the end of a hollow rod (Fig. 129) and blowing this into the form of large hollow cylinders (Fig. 130) about 6 ft. long and 1½ ft. in diameter. These are cut longitudinally (Fig. 131), and are then placed in an oven and heated until they soften, when they are flattened out into plates and cut into the desired sizes. Similar cylinders are now made by dipping a hollow tube into the melted glass and slowly withdrawing it while compressed air is blown through the tube. In this way a very long cylinder is formed. Plate glass is cast into flat slabs (Fig. 132), which are then ground and polished (Fig. 133) to perfectly plane surfaces.

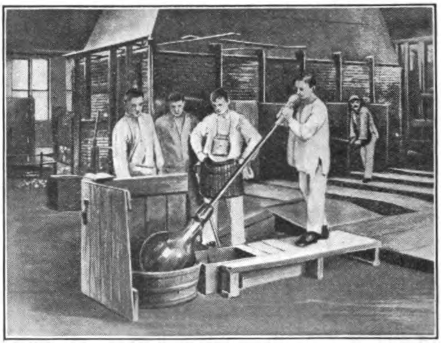


Fig. 129. First step in making window glass: blowing the ball

Varieties of glass. The glass made from sodium carbonate, lime, and sand is soft and easily fusible. If potassium carbonate is substituted for the sodium carbonate, the glass is much harder and less easily fused; increasing the amount of sand has somewhat the same effect. Potassium glass, of which *Jena* glass is a variety, is largely used in making chemical glassware, since it resists the action of reagents better than the softer sodium glass. If lead oxide is substituted for the whole or a part of the lime, the glass is very soft, but has a high index of refraction and is valuable for making optical instruments and artificial jewels (paste).

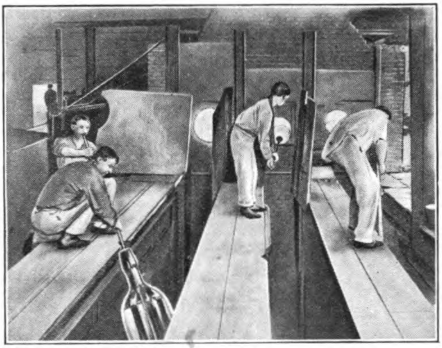


Fig. 130. Second step in making window glass: blowing the cylinders

Coloring glass. Various substances fused along with the glass give characteristic colors. The amber color of common bottles is due to iron compounds in the glass; in other cases iron colors the glass green. Cobalt compounds color it deep blue; compounds of manganese give it an amethyst tint, and uranium compounds impart a peculiar yellowish-green color. Iron is nearly always present in sand, and this makes a green glass unless

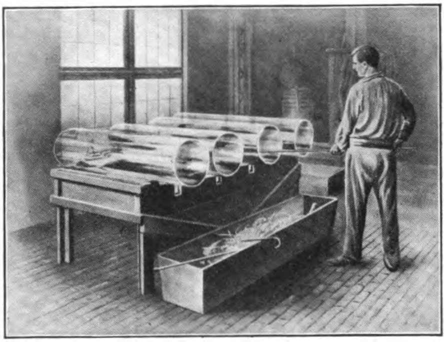


Fig. 131. Third step in making window glass: cutting the cylinders

an oxidizing agent is used. The green color is largely removed by the addition of manganese dioxide, which oxidizes the iron to a form having a yellowish tinge, and this color is then neutralized by the manganese, since the yellow produced by the iron and the amethyst produced by the manganese are complementary colors, producing white light.

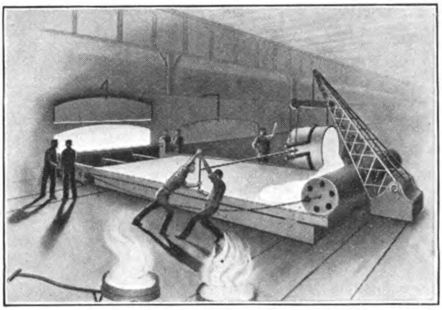


FIG. 132. Casting plate glass

Nature of glass. Glass is not a definite chemical compound, and its composition varies between wide limits. Fused glass is really a solution of various silicates, such as those of calcium and lead, in fused sodium silicate or potassium silicate. A certain amount of silicon dioxide is also present. This solution is cooled under such conditions that the dissolved substances do not separate from the solvent. The compounds which are used to color the glass are sometimes converted into silicates which then dissolve in the glass, giving it a uniform color. In other cases, as in the *milky* glasses which resemble porcelain in appearance, the color or opaqueness is due to the finely divided material evenly distributed throughout the glass, but not dissolved in it. Milky glass is made by mixing calcium fluoride, tin oxide, or some other insoluble substance in the melted glass. Selenium or gold in very finely divided (colloidal) form scattered through glass gives it shades of red.

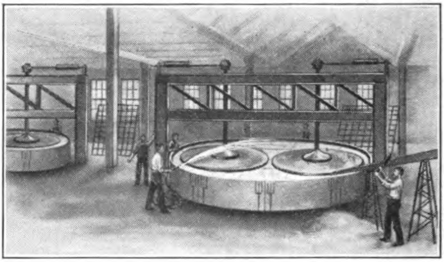


FIG. 133. Polishing plate glass

Enamels. The surface of metal vessels, such as cooking utensils and bath tubs, is often covered by a kind of opaque glass called *enamel* (granite or agate ware). This contains boric oxide (B_2O_3) in place of some silica, and oxides of a number of different metals, such as barium, zinc, or lead, in place of some of the calcium.

BORON

Occurrence. Boron occurs in nature as *boric acid* (H_3BO_3), and in salts of *polyboric acids*, which usually have very complicated formulas.

Preparation and properties. The element boron is extremely difficult to prepare in pure condition, and it is only known in an amorphous state. Its electrical resistance varies to an extraordinary extent with changes in temperature, and this property promises to make it very useful.

Boric acid (H_3BO_3). This compound is found dissolved in the water of hot springs in some localities, particularly in Italy. Being volatile with steam, boric acid is present in the vapor from these springs. The acid is easily obtained from these sources by condensation and evaporation, the necessary heat being supplied by other hot springs.

It is often prepared by treating a strong, hot solution of borax ($Na_2B_4O_7$) with sulfuric acid. Boric acid, being but sparingly soluble in water, crystallizes out on cooling:

$$Na_2B_4O_7 + 5\,H_2O + H_2SO_4 \longrightarrow Na_2SO_4 + 4\,H_3BO_3$$

Boric acid crystallizes in pearly flakes which are slippery to the touch. It is a mild antiseptic, and is often used in medicine, particularly for eyewashes. Its acid properties are extremely weak.

Metaboric and polyboric acids. When boric acid is gently heated, it is converted into metaboric acid (HBO_2):

$$H_3BO_3 \longrightarrow HBO_2 + H_2O$$

On heating metaboric acid to a somewhat higher temperature, tetraboric acid ($H_2B_4O_7$) is formed:

$$4\,HBO_2 \longrightarrow H_2B_4O_7 + H_2O$$

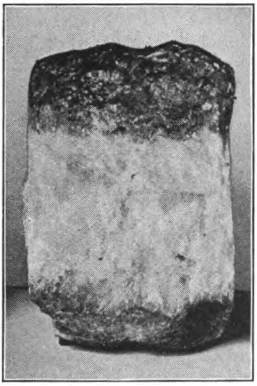


FIG. 134. A specimen of colemanite

Borax. The sodium salt of tetraboric acid has the formula $Na_2B_4O_7$. Borax is a hydrate (p. 271) of this salt. It is found in some arid countries, as southern California and Tibet, but is now made commercially from the mineral *colemanite.* This is the calcium salt of a complex boric acid ($Ca_2B_6O_{11}$) and occurs in large deposits in California. When it is treated with a solution of sodium carbonate, calcium carbonate is precipitated and borax crystallizes from the solution. Fig. 134 shows a sample of colemanite, and Fig. 135 the crystalline borax obtained from it.

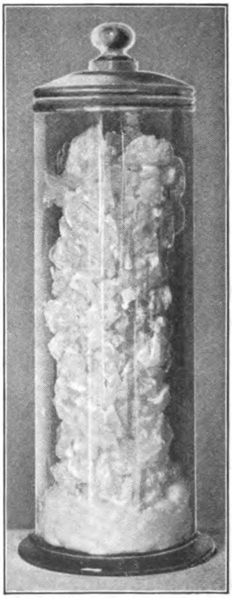


FIG. 135. Crystals of borax

When heated, borax at first swells up greatly, and then melts to a clear glass. This glass has the property of easily dissolving many metallic oxides, and on this account borax is used as a flux in brazing, for the purpose of removing from the metallic surfaces to be brazed the film of oxide with which they are likely to be covered (p. 272). These oxides often give a characteristic color to the clear borax glass, and on this account borax beads are often used in testing for the presence of metals.

Borax is extensively used as a constituent of enamels and glazes for both metal ware and pottery. It is used to soften hard water for domestic purposes (p. 300), as a mild alkali (like soap), as an antiseptic, and as a flux in brazing.

Hydrates; water of hydration. The water with which any compound unites to form a hydrate is termed *water of hydration.* In writing the formula of a hydrate it is customary to represent the water of hydration separately. Thus, the formula of borax is written $Na_2B_4O_7 \cdot 10\,H_2O$. This expresses the fact that 1 molecule of borax is made up of 1 molecule of sodium tetraborate ($Na_2B_4O_7$) and 10 molecules of water of hydration. The hydrates are true chemical compounds, and most of them are crystalline. When a hydrate is heated, the water of hydration is driven off. A salt crystallizing without water of hydration is said to be *anhydrous.*

EXERCISES

1. Account for the fact that both silicon and carborundum can be made by heating sand with carbon.
2. Account for the fact that a solution of borax in water is alkaline.
3. What weight of water of hydration does 1 kg. of borax contain? *Ans.* 471 g.
4. What weight of borax can be made from a ton of colemanite? *Ans.* 3559 lb.
5. Why does not sodium silicate form a glass suitable for common use?

TOPICS FOR THEMES

Glass-making (Rogers and Aubert, Industrial Chemistry).

Death Valley and the borax beds (see encyclopedia).

CHAPTER XXVIII

THE METALS

The metals. The elements so far considered have nearly all been those whose compounds with oxygen and hydrogen are *acids*, and they are called the *acid-forming* elements. Those which we shall now study are known collectively as the *metals*. Their hydroxides are *bases*, and on this account the *metals are sometimes defined as those elements whose hydroxides are bases.* When the hydroxide of a metal or any of the simple salts derived from the hydroxide are dissolved in water, the metallic element forms the cation and carries a positive charge.

Properties of the metals. The metals are all solids, except mercury, which is a liquid. Most metals have a high density, are good conductors of heat and electricity, are notably crystalline in structure, and take a bright polish. With the exception of gold and copper, they have a silvery luster. Most of them combine readily with oxygen and sulfur, and their surfaces quickly tarnish on exposure to the air.

A few of the least active of the metals, such as gold and copper, occur to some extent in nature in the native state. Most of them are found in combination as *oxides*, as *sulfides*, or as salts of various acids, especially as silicates. The process of winning metals from their ores is called *metallurgy*. The details of the metallurgy of any given metal must be adapted to the properties of the metal, to the form in which it is found, and to the cost of the operation.

Compounds of the metals. Since the metallic elements are base-forming elements, the compounds which they form are chiefly oxides, hydroxides, and salts of various acids. We may expect each metal to form a salt with each acid, and since a great many acids are known, the total number of salts is very great. Only those will be described which have important uses in the industries.

Preparation of salts. There are two general ways of preparing salts, which are employed so often that it is well to fix them in mind at the outset of the study of metals.

1. ***Soluble salts.*** If a given salt is *soluble*, it can usually be prepared in solution by treating the proper metal, or its oxide, hydroxide, or carbonate, with the proper acid. All of these reactions have already been illustrated repeatedly:

$$\begin{aligned} Cu + 2\,H_2SO_4 &\longrightarrow CuSO_4 + SO_2 + 2\,H_2O \quad && \text{(p. 155)} \\ CuO + 2\,HNO_3 &\longrightarrow Cu(NO_3)_2 + H_2O && \text{(p. 129)} \\ NaOH + HCl &\longrightarrow NaCl + H_2O && \text{(p. 109)} \\ CaCO_3 + 2\,HCl &\longrightarrow CaCl_2 + H_2O + CO_2 && \text{(p. 198)} \end{aligned}$$

2. ***Insoluble salts.*** A very large number of salts are insoluble in water, and these can be made by *precipitation.* All that it is necessary to do is to bring together in solution two salts, one of which contains the desired metallic cation and the other the anion. If, for example, it is known that silver chloride is insoluble in water, it is to be expected that this salt will be precipitated on bringing together in solution a soluble silver salt ($AgNO_3$) and a soluble chloride ($NaCl$):

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

If the desired salt is also *insoluble in strong acids*, it may be prepared by treating a soluble salt with the proper acid:

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\,HCl$$

Electrochemical industries. To an ever-increasing extent electrical energy is being used both in the separation and refining of the metals and for the production of many compounds. Such methods have in a number of instances already been mentioned. Naturally these industries tend to develop most extensively in localities where water power is abundant. Norway has many electrochemical industries. Those of the United States and Canada center at Niagara Falls, the extensive power plants being shown in Fig. 136.

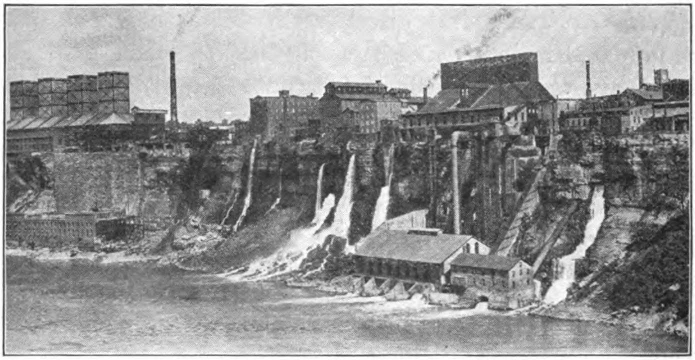


FIG. 136. Electrochemical power plants at Niagara Falls

Solubility of salts. It will be seen that a knowledge of the solubility of various salts is of great importance if one wishes to devise a means of preparing a given salt. Fortunately it is possible to put into brief form the facts relating to the solubility of the common salts, and these rules will have constant application in the pages which follow.

1. ***Hydroxides.*** All *hydroxides are insoluble* except those of ammonium, sodium, potassium, calcium, barium, and strontium.
2. ***Nitrates.*** All *nitrates are soluble.*

3. ***Chlorides.*** All *chlorides are soluble* except silver and mercurous chlorides. (Lead chloride is but slightly soluble.)

4. ***Sulfates.*** All *sulfates are soluble* except those of lead, barium, and strontium. (Sulfates of silver and calcium are only moderately soluble.)

5. ***Sulfides.*** All *sulfides are insoluble* except those of ammonium, sodium, and potassium. The sulfides of calcium, barium, strontium, and magnesium are insoluble in water, but are changed by hydrolysis into acid sulfides which are soluble. On this account they cannot be prepared by precipitation.

6. ***Carbonates, phosphates, and silicates.*** All normal *carbonates, phosphates, and silicates are insoluble* except those of ammonium, sodium, and potassium.

EXERCISES

1. Devise reactions for the preparation of the following *soluble* salts: $Ca(NO_3)_2$, $CuSO_4$, $ZnCl_2$, $FeSO_4$, and KNO_3.

2. Devise reactions for the preparation of the following *insoluble* salts: $PbSO_4$, $HgCl$, $CaCO_3$, $Fe(OH)_3$, $BaSO_4$.

3. How does water power aid in the electrochemical industries?

4. In what processes already studied is the electric current used?

CHAPTER XXIX

THE SODIUM FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	FIRST PREPARED
Lithium	Li	6.94	0.534	186°	Arfvedson, 1817
Sodium	Na	23.00	0.971	97°	Davy, 1807
Potassium	K	39.10	0.862	62°	Davy, 1807
Rubidium	Rb	85.45	1.53	38°	Bunsen, 1861
Cæsium	Cs	132.81	1.87	26°	Bunsen, 1861

The family. The metals appearing in the above table constitute a family in Group I in the periodic arrangement of the elements. The name *alkali metals* is often applied to the family for the reason that the hydroxides of the most familiar members of the family (namely, sodium and potassium) have long been called *alkalis.* The alkali metals are all readily acted upon both by air and by water, and are not found in a free state in nature. Sodium and potassium are the only important members of the family.

SODIUM

Occurrence. Large deposits of sodium chloride have been found in various parts of the world, and the water of the ocean and of many lakes and springs contains notable quantities of it. The element also occurs as a constituent of many rocks, and its compounds are therefore present in the soil formed by their disintegration. The nitrate, the carbonate, the borate, and many silicates also occur in nature.

Preparation. Formerly sodium was prepared by reducing the carbonate with carbon:

$$Na_2CO_3 + 2\,C \longrightarrow 2\,Na + 3\,CO$$

At present it is prepared by the electrolysis of the melted hydroxide or chloride. Water must be excluded; otherwise the sodium, as fast as it is liberated, will react with the water to form sodium hydroxide.

Technical preparation. The sodium hydroxide is melted in a cylindrical iron vessel *A* (Fig. 138) through the bottom of which rises the cathode *B*. The anodes *C*, several in number, are suspended around the cathode from above. A cylindrical vessel *E* floats in the fused alkali, directly over the cathode, and under this cap the sodium and hydrogen liberated at the cathode collect. The hydrogen escapes by lifting the cover, and the sodium, protected from the air by the hydrogen, is from time to time skimmed or drained off. Oxygen is set free upon the anode and escapes into the air through the opening *F* without coming into contact with the sodium or the hydrogen.

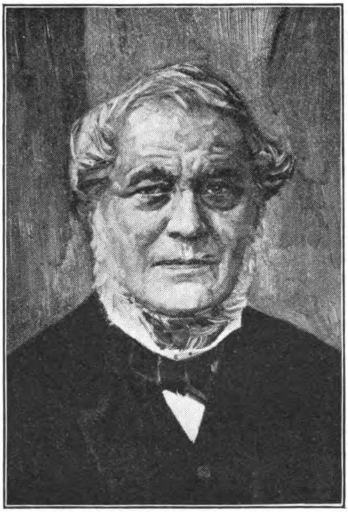


FIG. 137. Robert Wilhelm Bunsen (1811–1899)

A distinguished German chemist who discovered rubidium and cæsium, invented the laboratory burner, and contributed to many advances in chemistry

Properties. Sodium is a silver-white metal about as heavy as water, and so soft that it can be molded easily by the fingers or pressed into wire. It is very active chemically, combining with most of the nonmetallic elements, such as oxygen and chlorine, with great energy. It will often displace hydrogen or metals combined with other elements (p. 112), and is thus able to decompose water and the oxides and chlorides of many metals. It forms many useful compounds, nearly all of which are soluble in water.

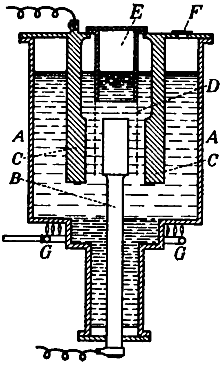


FIG. 138. An electrolytic cell for the preparation of sodium

Sodium peroxide (Na_2O_2). Since sodium is a univalent element, we should expect it to form an oxide of the formula Na_2O. While such an oxide can be prepared, the peroxide, Na_2O_2, is much better known. This is a yellowish-white powder made by burning sodium in air. Its chief use is as an oxidizing agent. When heated with oxidizable substances, it gives up a part of its oxygen, as shown in the equation

$$Na_2O_2 \longrightarrow Na_2O + [O]$$

When sodium peroxide is brought into contact with water, oxygen is evolved. On this account it is sometimes used in the preparation of oxygen:

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

Sodium hydroxide (caustic soda) (NaOH). Sodium hydroxide is prepared commercially by several processes.

1. In the older process, still in extensive use, sodium carbonate is treated with calcium hydroxide. Calcium carbonate is precipitated according to the equation

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2\,NaOH$$

The dilute solution of sodium hydroxide, filtered from the calcium carbonate, is evaporated to a paste and then poured into molds to solidify. It is sold in the form of slender sticks.

2. The newer methods depend upon the electrolysis of sodium chloride:

$$2\,NaCl + 2\,H_2O \longrightarrow 2\,NaOH + H_2 + Cl_2$$

The chief difficulty in this process is to prevent the resulting sodium hydroxide and chlorine from coming in contact and acting upon each other. This difficulty is overcome by separating the cathode compartment (in which the sodium hydroxide is produced) from the anode compartment (in which the chlorine is evolved) by means of a porous partition.

Properties. Sodium hydroxide is a brittle, white crystalline substance which rapidly absorbs water and carbon dioxide from the air. As the name *caustic soda* indicates, it is a very corrosive substance, having a disintegrating action on most animal and vegetable tissues. In solution it is a strong base. It is used in a great many chemical industries, its chief use being in the manufacture of soap (p. 291). As a household article it is sold under the name of *lye.*

Sodium chloride (common salt) (NaCl). Sodium chloride, or common salt, is very widely distributed in nature. Thick strata, evidently deposited by the evaporation of salt water, are found in many places. In the United States the most important localities for salt are New York, Michigan, Ohio, and Kansas. Sometimes the salt is mined, especially if it is in the pure form called *rock salt.* More frequently a strong brine is pumped from deep wells sunk into the salt deposit. The brine is evaporated either by heating or, in the preparation of the coarser grades of salt, by simply exposing the brine to the air (Fig. 139). Salt crystallizes in the form of small cubes.

Uses of salt. Since salt is so abundant in nature, it is used in the preparation of nearly all compounds containing either sodium or chlorine. These include many substances of the highest importance to civilization, such as soap, glass, hydrochloric acid, soda, and bleaching powder. Enormous quantities of salt are therefore produced each year. Small quantities are essential to the life of man and animals. Pure salt does not absorb moisture; the fact that ordinary salt becomes moist when exposed to air is not due to a property of the salt but to impurities occurring in it, especially to the presence of calcium and magnesium chlorides.

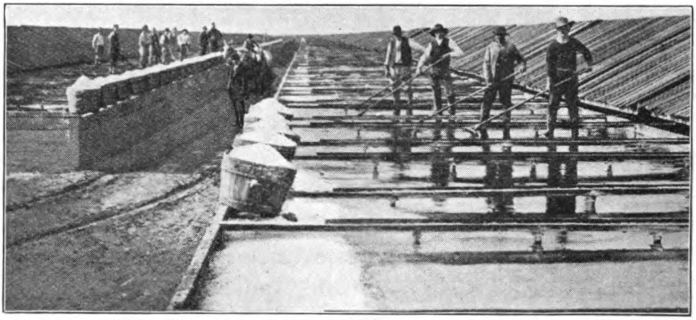


FIG. 139. The evaporation of salt brine in the open air (New York State)

Sodium sulfate (Na_2SO_4). This salt is prepared by the action of sulfuric acid upon sodium chloride, hydrogen chloride being formed at the same time (p. 175):

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl$$

The anhydrous salt is a white solid. It is readily soluble in water, and under ordinary conditions crystallizes out as the hydrate $Na_2SO_4 \cdot 10\,H_2O$ (known as *Glauber's salt*). Large quantities of sodium sulfate are used in making sodium carbonate and glass. The salt is also used in medicine.

Sodium carbonate (Na_2CO_3). There are two different methods now employed in the manufacture of this salt.

1. ***Leblanc process.*** This older process involves several distinct reactions, as shown in the following equations:

a. Sodium chloride is first converted into sodium sulfate:

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl$$

b. The sodium sulfate is next reduced to sulfide by heating it with carbon:

$$Na_2SO_4 + 2\,C \longrightarrow Na_2S + 2\,CO_2$$

c. The sodium sulfide is then heated with calcium carbonate, when the following reaction takes place:

$$Na_2S + CaCO_3 \longrightarrow CaS + Na_2CO_3$$

2. ***Solvay process.*** This more modern process depends upon reactions taking place *in solution*, and represented in the equations

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl \qquad (1)$$
$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \qquad (2)$$

When concentrated solutions of sodium chloride and of ammonium hydrogen carbonate are brought together, the sparingly soluble sodium hydrogen carbonate is precipitated as represented in equation (1). This, by heating, is converted into the normal carbonate as indicated in equation (2). The ammonium chloride formed (equation (1)) is treated with lime (p. 122), ammonia being liberated. This ammonia, together with water and the carbon dioxide generated as indicated in equation (2), combine to form ammonium hydrogen carbonate,

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$$

This is treated with salt, and the process is begun over again.

Historical. In former times sodium carbonate was made by burning seaweeds and extracting the carbonate from their ash. On this account the salt was called *soda ash*, and the name is still in common use. During the French Revolution this supply was cut off, and in behalf of the French government Leblanc (Fig. 140) made a study of methods of preparing the carbonate directly from salt. As a result he devised the method which bears his name, and which was used exclusively for many years. It has been replaced to a large extent by the Solvay process, which was devised by the Belgian chemist Solvay in 1863.

FIG. 140. Nicolas Leblanc (1742–1806)

Inventor of the first method of preparing sodium carbonate from salt. (Statue erected in Paris)

By-products. The substances obtained in a given process, aside from the main product, are called the *by-products.* The success of many processes depends upon the value of the by-products formed. Thus, hydrochloric acid, a by-product in the Leblanc process, is valuable enough to make the process pay, even though sodium carbonate can be made more cheaply in other ways.

Properties of sodium carbonate. Sodium carbonate forms large crystals of the formula $Na_2CO_3 \cdot 10\,H_2O$, known as *washing soda*, or *sal soda.* Its solution in water has a mild alkaline reaction, and is used for laundry purposes. Mere mention of the fact that it is used in the manufacture of glass, soap, and many chemical reagents will indicate its importance in the industries. It is one of the few soluble carbonates.

Sodium hydrogen carbonate ($NaHCO_3$). This salt, called *bicarbonate of soda*, or *baking soda*, is made by the Solvay process, as explained above, or by passing carbon dioxide into concentrated solutions of sodium carbonate:

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2\,NaHCO_3$$

It is an essential constituent of all baking powders (p. 330).

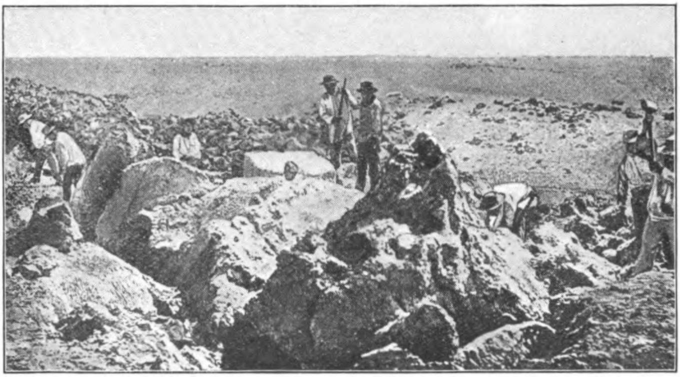


FIG. 141. A sodium nitrate deposit in Chile

Sodium nitrate ($NaNO_3$). This substance, known also as *Chile saltpeter*, is found in nature in certain arid regions, where apparently it has been formed by the decay of organic substances in the presence of air and sodium salts. The largest deposits are in Chile, and most of the nitrate of commerce comes from that country. Fig. 141 shows a deposit of sodium nitrate in Chile after it has been broken apart by explosives. Smaller deposits occur in California and Nevada. The commercial salt is prepared by dissolving the crude nitrate (known as *caliche*) in water, allowing the insoluble earthy materials to settle, and evaporating to crystallization the clear solution so obtained. The soluble impurities remain for the most part in the mother liquors.

Since this salt is the only nitrate found extensively in nature, it is the material from which other nitrates, as well as nitric acid, are prepared. Enormous quantities are used as a fertilizer and in the manufacture of sulfuric acid.

Sodium thiosulfate ($Na_2S_2O_3$). This salt is made by boiling a solution of sodium sulfite with sulfur:

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

The hydrate $Na_2S_2O_3 \cdot 5\,H_2O$ is frequently called *sodium hyposulfite*, or simply *hypo.* It is used in photography (p. 367), and in the bleaching industry to absorb the excess of chlorine which is left upon the bleached fabrics.

Other compounds of sodium. (1) *Sodium sulfite* (Na_2SO_3). (2) *Normal sodium phosphate* (Na_3PO_4). This salt readily hydrolyzes, forming a basic solution. (3) *Disodium phosphate* (Na_2HPO_4). This is the most common of the phosphates of sodium, and is usually known simply as sodium phosphate.

POTASSIUM

Occurrence. Potassium is a rather abundant element, being a constituent of many igneous rocks, such as the feldspars and micas. Very large deposits of the chloride and the sulfate, associated with compounds of calcium and magnesium, are found at Stassfurt, Germany, and are known as the *Stassfurt salts.*

The natural decomposition of rocks containing potassium gives rise to various compounds of the element in all fertile soils. Its soluble compounds are absorbed by growing plants and built up into complex vegetable tissues; when these are burned, the potassium remains in the ash in the form of carbonate. The crude carbonate can be separated from wood ashes by dissolving it in water. This was formerly the chief source of potassium compounds, but they are now prepared mostly from the salts of the Stassfurt deposits.

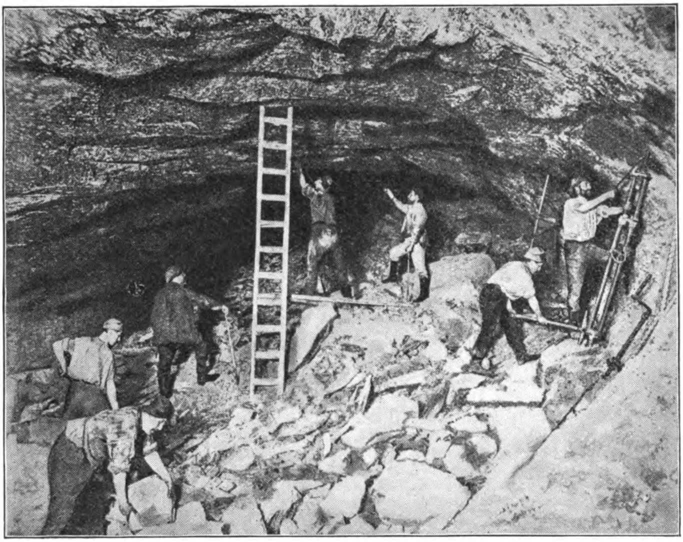


FIG. 142. Mining Stassfurt salts for use in the manufacture of fertilizers

Potassium in sea plants. While sodium rather than potassium is likely to be present in sea plants, nevertheless some of these plants, such as the giant algæ of the California coast, contain potassium chloride, amounting in some cases to 30 per cent of their dry weight. It is thought that perhaps these may constitute a commercial source of potassium compounds, large quantities of which are used in fertilizers. At present, however, the Stassfurt salts constitute by far the cheapest source, although the dried algæ are being used to some extent as a fertilizer.

Stassfurt salts. These salts form very extensive deposits in middle and north Germany, the most noted locality for working them being at Stassfurt. The deposits are very thick and rest upon an enormous layer of common salt. They are in the form of a series of strata, each consisting largely of a single mineral salt. While these strata are salts from a chemical standpoint, they are as solid and hard as many kinds of stone and are mined as stone or coal would be (Fig. 142). The chief minerals of commercial importance in these deposits are the following:

Sylvite	KCl
Kainite	$KCl \cdot MgSO_4 \cdot 3\,H_2O$
Carnallite	$KCl \cdot MgCl_2 \cdot 6\,H_2O$
Kieserite	$MgSO_4 \cdot H_2O$

Preparation and properties. Potassium is prepared by methods similar to those used in the preparation of sodium. It is more active than sodium; otherwise the properties of the two metals are alike.

Compounds. The compounds of potassium are so similar in properties to the corresponding compounds of sodium that for many purposes for which they are used they can be interchanged. The compounds of potassium, being as a rule more expensive, are not so widely used as those of sodium.

Potassium hydroxide (caustic potash) (KOH). Potassium hydroxide is prepared by methods exactly similar to those used in the preparation of sodium hydroxide, which compound it closely resembles in both physical and chemical properties. It is not used to any very great extent, being replaced by the cheaper sodium hydroxide.

Action of the halogen elements on bases. When any one of the three halogen elements — chlorine, bromine, or iodine — is added to a solution of a base such as the hydroxide of sodium, of potassium, or of calcium, a reaction takes place, the nature of which depends upon the temperature. Thus, when chlorine is passed into a *cold* solution of potassium hydroxide, the reaction expressed by the following equation takes place:

$$2\,KOH + Cl_2 \longrightarrow KCl + KClO + H_2O \qquad (1)$$

If the solution of hydroxide is *hot*, the potassium hypochlorite (KClO) formed according to equation (1) breaks down as fast as formed:

$$3\,KClO \longrightarrow KClO_3 + 2\,KCl \qquad (2)$$

By means of these reactions one can prepare the chloride, hypochlorite, and chlorate of sodium, of potassium, and of calcium. By substituting bromine or iodine for chlorine the corresponding compounds of those elements are obtained. Some of these compounds can be obtained in cheaper ways.

Potassium chlorate ($KClO_3$). This salt, as has just been explained, can be made by the action of chlorine on concentrated solutions of potassium hydroxide. It is a white crystalline substance, and is used chiefly as an oxidizing agent in the manufacture of matches, fireworks, and explosives; it is also used in the preparation of oxygen and in medicine.

Potassium nitrate ([redacted]) (KNO_3). This salt is found native in some regions where the climate is hot and dry, being formed by the decay of nitrogenous organic matter in the presence of earthy material containing potassium. The saltpeter used in making gunpowder was formerly made by imitating these conditions. At present it is prepared by the action of sodium nitrate upon potassium chloride (the former compound being obtained from Chile and the latter from the Stassfurt deposits):

$$NaNO_3 + KCl \longrightarrow KNO_3 + NaCl$$

Potassium nitrate is a white solid. It is an excellent oxidizing agent, and its chief use is in the manufacture of gunpowder (p. 294). For this purpose it is preferable to sodium nitrate, since the latter is slightly deliquescent and powder made from it, if exposed to air, soon becomes moist and unfit for use. Small amounts of the nitrate are also used in medicine and as a preservative for meats, especially for corned beef.

Other compounds of potassium. *Potassium chloride* (KCl), *potassium bromide* (KBr), and *potassium iodide* (KI) are all white solids. The bromide and the iodide are both used in the preparation of photographic reagents and in medicine. *Potassium carbonate* (K_2CO_3), *potassium bicarbonate* ($KHCO_3$), *potassium sulfate* (K_2SO_4), and *potassium bisulfate* ($KHSO_4$) are all well-known compounds. They are white solids, readily soluble in water.

THE AMMONIUM COMPOUNDS

Composition. As explained in a previous chapter, when ammonia is passed into water the two combine to form the base NH_4OH, known as *ammonium hydroxide.* When this base is neutralized with acids, there are formed the corresponding salts, known as the *ammonium salts.* Since the ammonium radical is univalent, ammonium salts resemble those of the alkali metals in their formulas; they also resemble the latter salts very much in their chemical properties, and may be conveniently described in connection with them. Among the ammonium salts the chloride, sulfate, carbonate, and sulfide are the most familiar.

Ammonium chloride (sal ammoniac) (NH_4Cl). This is a white solid. When heated it partly decomposes into ammonia and hydrogen chloride, which recombine, as the temperature falls:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

This salt is used in soldering, since the hydrogen chloride evolved by the heat removes the oxide from the surface of the metals. It is also used in making dry cells, in medicine, and as a chemical reagent.

Ammonium sulfate ($(NH_4)_2SO_4$). This salt is prepared at low cost, and is especially valuable as a fertilizer.

The carbonates of ammonium. Both the normal carbonate $(NH_4)_2CO_3$ and the acid carbonate NH_4HCO_3 are white solids, readily soluble in water. The normal carbonate slowly decomposes into the acid carbonate, evolving ammonia:

$$(NH_4)_2CO_3 \longrightarrow NH_4HCO_3 + NH_3$$

Both carbonates are used as chemical reagents.

Ammonium sulfides. When hydrogen sulfide is passed into aqua ammonia, a solution containing ammonium sulfide ($(NH_4)_2S$) and ammonium acid sulfide (NH_4HS) is obtained:

$$NH_4OH + H_2S \longrightarrow NH_4HS + H_2O$$
$$2\,NH_4OH + H_2S \longrightarrow (NH_4)_2S + 2\,H_2O$$

This solution is usually known simply as ammonium sulfide, and is used as a reagent in testing for certain metals. When exposed to the air it slowly decomposes, and the sulfur liberated in the process combines with the compounds present, forming different sulfides, such as $(NH_4)_2S_2$ and $(NH_4)_2S_3$, or, in general, $(NH_4)_2S_x$. The resulting solution is yellow and is termed *yellow ammonium sulfide* or *ammonium polysulfide*.

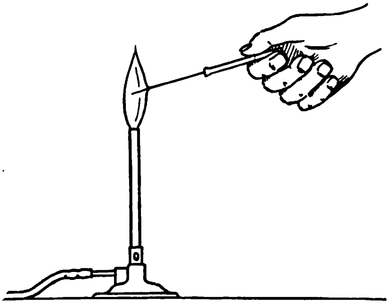


FIG. 143. Method of making a flame test

Flame reactions. A number of the metals, when volatilized in a colorless flame, such as that of a Bunsen burner, impart a characteristic color to the flame. Thus, sodium (or any of its compounds that will volatilize in the heat of the flame) imparts to the flame a strong yellow color. Potassium and its compounds color the flame a pale violet, and lithium colors it a deep crimson red.

Advantage is taken of these facts in testing for the presence of the elements in different substances. The test is best made by using a platinum wire, one end of which is fused into a piece of glass tubing that serves as a handle. The other end of the wire is dipped into water and rubbed in the substance to be tested (or dipped into a concentrated solution of the substance), and the wire with the adhering particles is held in the outer edge of the base of the Bunsen flame (Fig. 143).

EXERCISES

1. What is an alkali? What does the word *alkali* signify (see dictionary)? Can a metal itself be an alkali?

2. What carbonates are soluble?

3. Account for the fact that solutions of sodium carbonate and potassium carbonate are basic.

4. What nonmetallic element is obtained from the deposits of Chile saltpeter?

5. What would take place if a bit of potassium hydroxide were left exposed to the air?

6. What substances already studied are prepared from the following compounds: ammonium chloride; ammonium nitrate; ammonium nitrite; sodium nitrate?

7. What weight of sal soda can be prepared from 1 ton of salt? *Ans.* 4894.9 lb. What weight of it is water of hydration? *Ans.* 3081.8 lb.

TOPICS FOR THEMES

The kelp industry (Roscoe and Schorlemmer, Chemistry; see also encyclopedia).

The Stassfurt deposits (Roscoe and Schorlemmer, Chemistry; see also encyclopedia).

The salt wells of the United States. (Write to your state geologist for sources of information.)

CHAPTER XXX

SOAP; GLYCERIN; EXPLOSIVES

Composition of soap, and materials used in its preparation. Soap is a mixture of the sodium and potassium salts of oleic, palmitic, and stearic acids. The essential materials used in the preparation of soap are as follows:

1. ***Fat or oil.*** As shown on page 237, fats and oils are largely mixtures of olein, palmitin, and stearin. The cheaper grades of these are used in making soap. Those commonly employed are a low grade of animal fat (tallow) and the cheaper vegetable oils, such as cottonseed oil, coconut oil, and palm oil.

A low-grade fat obtained from garbage is also used in making soap and candles. When the garbage is heated with water, the fat rises to the top and is skimmed off. The remaining matter is used as a constituent of fertilizers.

2. ***Alkali.*** The alkali used is the hydroxide of either sodium or potassium. Sodium hydroxide is nearly always used, since it gives a hard soap, while potassium hydroxide gives a soft soap.

Reaction taking place in the preparation of soap. When the fat and alkali are heated together under proper conditions, the olein, palmitin, and stearin present in the fat are decomposed, forming glycerin, together with sodium oleate, sodium palmitate, and sodium stearate. A mixture of these three salts constitutes soap. The reactions may be illustrated by the following equation, which represents the change taking place when stearin is heated with sodium hydroxide :

$$\underset{\text{stearin}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{sodium hydroxide}}{3\,NaOH} \longrightarrow \underset{\text{glycerin}}{C_3H_5(OH)_3} + \underset{\text{sodium stearate}}{3\,NaC_{18}H_{35}O_2}$$

In this reaction the fat is said to be *saponified*, and the process is known as *saponification.*

Commercial manufacture of soap. The oil or melted fat is poured into large iron kettles together with a solution of sodium hydroxide containing about one fourth of the amount of alkali necessary to saponify the fat. As a rule, the kettles are very large (Fig. 144), 500,000 lb. or more of soap being made in some of them in a single heating. They are provided with coils of steam pipe for heating the mixture. The fat and alkali are stirred by forcing air or live steam into the bottom of the mixture. As the heating continues, the remainder of the alkali is added. The reaction is complete in from two to five days.

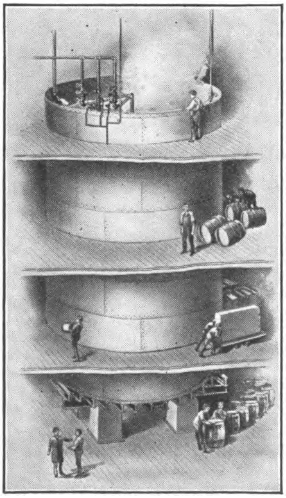


FIG. 144. A kettle used in making soap

The soap is next removed, or *salted out*, from the mixture. This process consists in adding salt and again heating. After a time the soap rises to the top of the liquid (or *spent lye*, as it is called). The soap so obtained is purified and then run into a mixing machine (crutcher). Here it is mixed with any appropriate material which it is desired to add, such as perfume, borax, sodium silicate, or sodium carbonate. It is then run into large molds to harden, after which it is cut and pressed into cakes of the desired size. The glycerin formed in the reaction is separated from the spent lye by distillation.

Varieties of soap. *Transparent soaps* are ordinarily made by dissolving soap in alcohol. The solution is filtered and the excess of alcohol removed by distillation. *Castile soaps* are made from mixtures of olive oil with cheaper oils. The color of *mottled soaps* is produced by the addition of ferrous sulfate, Prussian blue, or some similar pigment. *Floating soaps* owe their lightness to bubbles of air. *Naphtha soaps* contain from 5 per cent to 10 per cent of petroleum naphtha. *Scouring soaps* contain from 5 per cent to 10 per cent of soap and from 80 per cent to 90 per cent of some abrasive material such as fine sand or volcanic ash. Sometimes a small percentage of sodium carbonate is also present. *Soap powders* are, as a rule, sodium carbonate or a mixture of sodium carbonate and ground soap.

Properties of soap. Soap dissolves in soft waters, giving a slightly alkaline solution due to hydrolysis. If an acid, such as hydrochloric acid, is added to the aqueous solution, the organic acids are liberated from their salts and are precipitated in the form of white insoluble solids:

$$\underset{\text{sodium stearate}}{NaC_{18}H_{35}O_2} + HCl \longrightarrow NaCl + \underset{\text{stearic acid}}{H \cdot C_{18}H_{35}O_2}$$

The calcium and magnesium salts of oleic, palmitic, and stearic acids are insoluble in water, and are therefore precipitated when a calcium or magnesium compound is added to an aqueous solution of soap:

$$\underset{\text{sodium stearate}}{2\,NaC_{18}H_{35}O_2} + CaCl_2 \longrightarrow 2\,NaCl + \underset{\text{calcium stearate}}{Ca(C_{18}H_{35}O_2)_2}$$

It is due to this fact that soaps do not lather with hard waters but form a curdy precipitate, since such waters always contain calcium and magnesium salts in solution.

Cleansing action of soap. Attention has been called to the property possessed by soap of aiding in the formation of emulsions (Fig. 50). The cleansing power of soap is largely due to this fact. When soap is rubbed upon the skin, any oily substances present are emulsified by the soap solution and washed away.

Candles. When fats are heated with *steam*, they are decomposed into glycerin and free acid as follows:

$$\underset{\text{stearin}}{C_3H_5(C_{18}H_{35}O_2)_3} + 3\,H_2O \longrightarrow \underset{\text{glycerin}}{C_3H_5(OH)_3} + 3\,\underset{\text{stearic acid}}{H \cdot C_{18}H_{35}O_2}$$

The solid fatty acids thus obtained, mixed with paraffin, are used in making candles. The glycerin is easily separated, and this process and the process of soap-making constitute the commercial sources of this compound.

Glycerin ($C_3H_5(OH)_3$). This is a colorless oily liquid having a sweet taste. Nitric acid reacts with it just as with a base, forming the nitrate $C_3H_5(NO_3)_3$:

$$C_3H_5(OH)_3 + 3\,HNO_3 \longrightarrow C_3H_5(NO_3)_3 + 3\,H_2O$$

The nitric acid used in this reaction is mixed with a little sulfuric acid, the latter serving to absorb the water generated. Glycerin nitrate is a slightly yellowish oil commonly known as *nitroglycerin.* It is very explosive and is used in the manufacture of dynamite (p. 296).

Explosives. An explosion is caused by a very rapid chemical reaction which results in the formation of large volumes of gases from liquid and solid materials called *explosives.* The greater the volume change and the more rapidly it is produced, the more violent the explosion. The most common of the manufactured explosives are the following:

1. **Gunpowder.** Ordinary gunpowder is an intimate mixture of potassium nitrate, sulfur, and charcoal. When ignited, complicated reactions occur, the principal change being indicated in the following equation:

$$2\,KNO_3 + 3\,C + S \longrightarrow K_2S + 3\,CO_2 + N_2$$

The explosive effects are due to the sudden liberation of the highly heated carbon dioxide and nitrogen. The presence of the solid particles of the sulfide of potassium causes the smoke which accompanies the explosion.

2. **Nitrocellulose.** The nitrocellulose usually used in explosives has the formula $C_6H_7O_2(NO_3)_3$. This substance (p. 225) is a far more powerful explosive than gunpowder. If ignited, it will, under ordinary conditions, burn quietly. If subjected to a sudden shock (such as may be produced by the explosion of a small percussion primer), the nitrocellulose decomposes with enormous violence. The products of the decomposition are all colorless gases; hence the use of this explosive in making *smokeless* gunpowder. When used for this purpose, it is necessary to modify the pure material somewhat, as otherwise the violence of the explosion would shatter any firearms in which the powder was used. This is done by mixing nitrocellulose with sufficient alcohol and ether to form a plastic mass. This is then molded into the form of rods (grains) with a number of perforations through the rods. Fig. 145 shows the form of the grains used in the large guns of our navy.

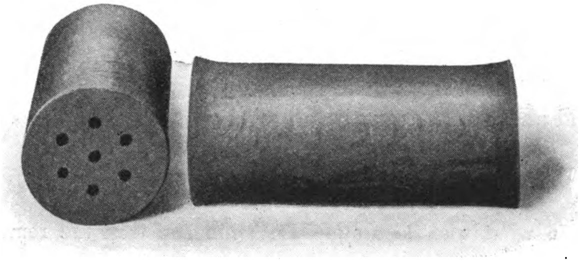


FIG. 145. Powder grains for large guns (natural size)

3. **Nitroglycerin ($C_3H_5(NO_3)_3$).** This resembles nitrocellulose in the violence of its explosive effects. The changes taking place in its decomposition are represented in a general way in the following equation:

$$4\,C_3H_5(NO_3)_3 \longrightarrow 12\,CO_2 + 6\,N_2 + 10\,H_2O + O_2$$

One volume of nitroglycerin yields on explosion about 1300 volumes of gas, which is expanded by the heat of the reaction to over 10,000 volumes. Pure nitroglycerin is very dangerous because of the ease with which it is set off. Large quantities are used in making dynamite, in which form it is not exploded so readily by jarring and can be transported with less danger. Ordinary *dynamite* consists of a mixture of sodium nitrate, nitroglycerin, and wood pulp, the latter acting as an absorbent for the nitroglycerin. *Gelatin dynamite* consists of nitrocellulose and nitroglycerin mixed together to form a jellylike mass. It is a very powerful explosive, since it contains no inert material.

4. **Trinitrotoluene ($C_7H_5(NO_2)_3$).** Recently the Germans have developed a powerful explosive known as trinitrotoluene. It is prepared by the action of nitric acid on toluene (p. 232). It is solid and can be transported with safety.

EXERCISES

1. In what way does aqua ammonia assist in the removal of grease?

2. For what is lye used as a household article?

3. What effect will the softening of a city water-supply have on soap consumption?

4. Why will gas which burns quietly in a stove explode violently if a sufficient quantity of it is allowed to escape into a room and is then ignited?

5. Give the steps in preparing nitroglycerin from garbage.

6. Why not use sodium nitrate in making gunpowder?

7. What are the approximate proportions in which the constituents of gunpowder are mixed in its preparation (see equation for reaction of explosion)?

8. Why are some gunpowders smokeless and others not?

TOPICS FOR THEMES

Soap-making (Rogers and Aubert, Industrial Chemistry).

Modern explosives (Bird, Modern Science Reader).

CHAPTER XXXI

THE CALCIUM FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MILLIGRAMS SOLUBLE IN 1 LITER OF WATER AT 18°		CARBONATE DECOMPOSES
				Sulfate	Hydroxide	
Calcium	Ca	40.07	1.55	2070.	1,670	At dull-red heat
Strontium	Sr	87.63	2.54	170.	7,460	At white heat
Barium	Ba	137.37	3.75	2.29	36,300	Scarcely at all

The family. The calcium family consists of the very abundant metal calcium and the rarer metals, strontium and barium. Like the alkali metals, they are acted upon by both water and air, and on this account do not occur in a free state in nature. They are bivalent, so that the formulas of their salts differ from the formulas of the corresponding salts of the alkali metals; moreover, their normal carbonates and phosphates are insoluble in water.

CALCIUM

Occurrence. Calcium is one of the abundant elements. In the form of a carbonate it occurs in a number of different forms, such as limestone and marble. The most important of its mineral compounds are the following:

Calcite	$CaCO_3$	Wollastonite .	$CaSiO_3$
Phosphorite . . .	$Ca_3(PO_4)_2$	Gypsum . . .	$CaSO_4 \cdot 2\,H_2O$
Fluorite	CaF_2	Anhydrite . .	$CaSO_4$

Preparation. Calcium is prepared commercially by the electrolysis of the melted chloride in the following way:

The apparatus consists of a cylindrical iron vessel (Fig. 146), through the bottom of which extends the iron cathode *A*. The anodes *B*, *B*, several in number, are placed about the sides of the vessel. The calcium separates in a molten condition at the cathode *A*, and rises in the form of globules to the lower surface of a solid stick of calcium *D*, suspended above the cathode. There it is chilled by a water-cooling device *C*, *C*, and adheres to the stick of calcium, which is slowly raised as it increases in length.

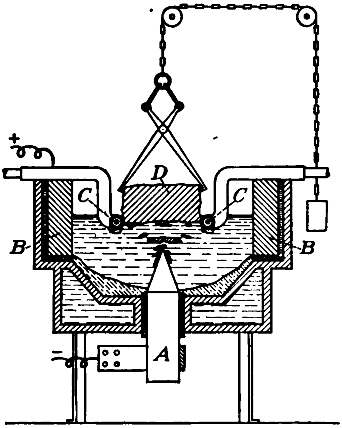


FIG. 146. The electrolytic preparation of calcium

Properties. Calcium is a silver-white metal which is only a little heavier than water. It is quite hard and melts at 810°. It combines readily with many of the elements, and when ignited, burns in oxygen with dazzling brilliancy. Like sodium and potassium, it decomposes water, forming a hydroxide and hydrogen. As yet it has few commercial applications.

Calcium carbonate ($CaCO_3$). Enormous quantities of calcium carbonate occur in nature. *Limestone* is the most abundant form, and sometimes constitutes whole mountain ranges. Limestone is never pure calcium carbonate, but contains variable percentages of magnesium carbonate, clay, silica, and compounds of iron. Pearls, coral, and various shells are largely calcium carbonate. *Calcite* is a very pure, crystalline form, and often is found in large transparent crystals (Fig. 147) called *Iceland spar*. *Marble* is composed of very small calcite crystals.

In the laboratory pure calcium carbonate can be prepared by treating a soluble calcium salt with a soluble carbonate:

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 + 2\,NaCl$$

When prepared in this way, it is a soft white powder often called *precipitated chalk*, and is much used as a polishing powder (tooth powder).

The natural varieties of calcium carbonate find many uses, as in the preparation of lime and of carbon dioxide; in metallurgical operations, especially in blast furnaces; in the manufacture of soda and glass; for building-stone and for ballast for roads.

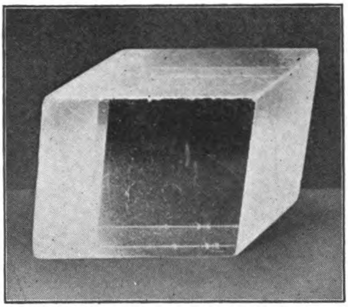


FIG. 147. A crystal of Iceland spar

Calcium acid carbonate ($Ca(HCO_3)_2$). Calcium carbonate is almost insoluble in pure water. It readily dissolves, however, in water which holds carbon dioxide in solution. This is due to the fact that the carbonate combines with the carbonic acid present in the water to form calcium acid carbonate, which is soluble:

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2$$

The resulting acid carbonate exists only in solution, since it is unstable and decomposes into the normal carbonate on heating or on evaporation of its solution.

Formation of caves. Natural waters always contain more or less carbon dioxide in solution. In the case of certain underground waters the amount of carbon dioxide is comparatively large, being held in solution by pressure. Such waters have a marked solvent action upon limestone, dissolving both the calcium carbonate and the magnesium carbonate. In certain localities this solvent action, continued through geological ages, has resulted in the formation in limestone rock of large caves, such as the Mammoth Cave in Kentucky. Water trickling through the roofs of these caves evaporates, leaving a deposit of calcium carbonate which, as the process continues, often forms icicle-shaped masses, known as *stalactites*; or the water may drip upon the floor of the cave, forming similar masses known as *stalagmites* (Fig. 148).

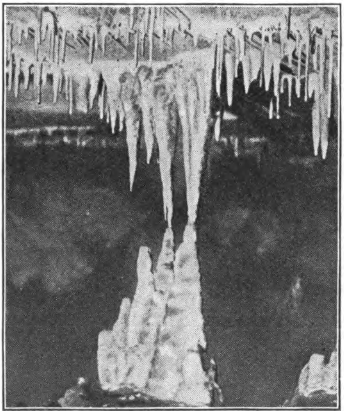


FIG. 148. Stalactites and stalagmites

Commercial methods for softening water. Hard waters contain not only the acid carbonates of magnesium and calcium but also the chlorides and sulfates of the metals, together with small quantities of other salts. On a small scale such waters are often softened by adding borax or normal sodium phosphate. These precipitate the calcium and magnesium present, at the same time leaving the water slightly alkaline and therefore adapted for cleaning purposes. On a large scale, as in the case of a city water-supply, the water is softened by the addition of calcium hydroxide and sodium carbonate. The calcium hydroxide converts the acid carbonates of calcium and magnesium into the normal carbonates, which, being insoluble, settle out:

$$CaHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2\,H_2O$$

The sodium carbonate used converts the chlorides and sulfates of calcium and magnesium into the insoluble carbonates:

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

Water softened in this way contains sodium sulfate and chloride, but these salts are not objectionable.

The amounts of calcium hydroxide and sodium carbonate required to soften any given water are calculated from an analysis of the water. These are added to the water in large tanks and thoroughly mixed. The mixture is then run out into settling basins. After the solids have settled, the clear water is drawn off.

Calcium oxide (lime) (CaO). Pure calcium oxide can be prepared by burning calcium or by heating its nitrate or carbonate. The more or less impure oxide (commercially known as *lime* or *quicklime*) is prepared by strongly heating limestone in large furnaces called *limekilns*:

$$CaCO_3 \longrightarrow CaO + CO_2$$

When pure, lime is a white amorphous substance. Heated intensely, as in the oxyhydrogen flame, it gives a brilliant light called the *limelight*. It is fusible only in the heat of the electric furnace. Water acts upon lime with the evolution of a great deal of heat, — whence the name *quicklime*, or *live lime*, — the process being called *slaking*. The equation is

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 15{,}540 \text{ cal.}$$

Because of its affinity for water it is used to dry gases. It also absorbs carbon dioxide, forming the carbonate:

$$CaO + CO_2 \longrightarrow CaCO_3$$

Lime exposed to air is therefore gradually converted into the hydroxide and the carbonate, and will no longer slake with water. It is then said to be *air-slaked.* Lime is produced in enormous quantities for use in making calcium hydroxide.

Commercial production of lime. A vertical section of the newer form of limekiln is shown in Fig. 149. The kiln is about 50 ft. in height. A number of fire boxes, or furnaces *A*, *A*, are built around the lower part, all leading into the central stack. The kiln is filled with limestone through a swinging door *B*. The hot products of combustion are drawn up through the kiln, and the limestone is gradually decomposed by the heat. The bottom of the furnace is so constructed that a current of air is drawn in at *C*, and this serves the double purpose of cooling the hot lime at the base of the furnace and of furnishing heated oxygen for the combustion. The lime is dropped into cars run under the furnace. Generally a number of these kilns are operated together, as shown in Fig. 150.

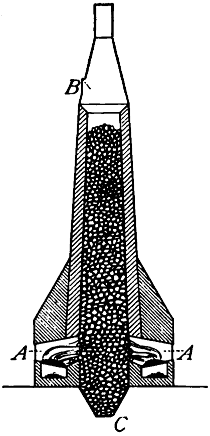


FIG. 149. Cross section of a modern limekiln

Calcium hydroxide (slaked lime) ($Ca(OH)_2$). This compound is prepared by adding water to lime, as explained above. When pure, it is a light white powder. It is sparingly soluble in water, forming a solution called *limewater.* Owing to its cheapness it is used in the industries whenever an alkali is desired. It is used in the preparation of ammonia, bleaching powder, and the hydroxides of sodium and potassium. It is also used to remove sulfur compounds and carbon dioxide from coal gas, to remove the hair from hides in making leather, for making mortar and plaster, and for liming soils (p. 110).

Mortar and plaster. Mortar is a mixture of calcium hydroxide and sand. When it is exposed to the air or spread upon porous materials, moisture is removed from it (partly by absorption into the porous materials and partly by evaporation) and the mortar becomes firm, or *sets*. At the same time carbon dioxide is slowly absorbed from the air and hard calcium carbonate is formed.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

By this combined action the mortar becomes very hard and adheres firmly to the surface upon which it is spread. The sand serves to give body to the mortar and makes it porous. It also prevents too much shrinkage. Plaster is a mixture of calcium hydroxide and hair, the latter serving to hold the mass together.

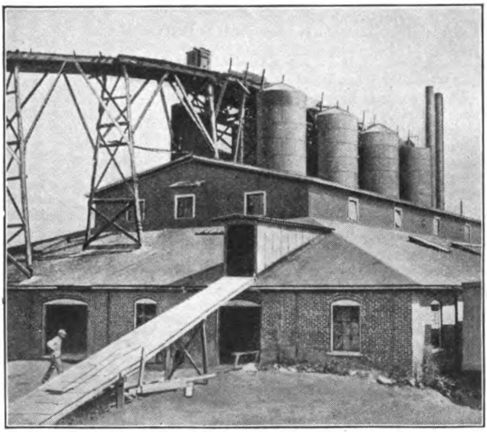


FIG. 150. A group of limekilns in a modern plant

Bleaching powder. When chlorine is passed over calcium hydroxide, there is formed a white solid compound having the formula $CaOCl_2$, and known as *bleaching powder*, *chloride of lime*, or simply *bleach*:

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

When this compound is treated with an acid, chlorine is evolved:

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

When exposed to the air, bleaching powder is slowly acted upon by moisture and carbon dioxide, with the liberation of hypochlorous acid ($HClO$), which is a good disinfectant.

Bleaching powder is prepared in large quantities for use as a bleaching agent, as a disinfectant, and as an agent for purifying city water-supplies.

In the commercial preparation of bleaching powder the calcium hydroxide is spread to a depth of 2 or 3 inches upon the floor of a room, usually made of lead or concrete (Fig. 151). The chlorine enters near the top at *A*. Any unabsorbed chlorine passes out at *B* and into the adjoining chamber at *C*.

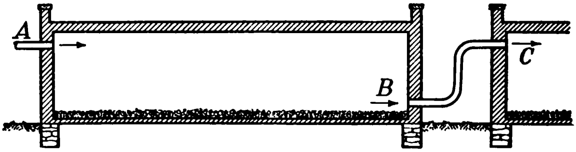


FIG. 151. Chambers for the manufacture of bleaching powder

Calcium sulfate ($CaSO_4$). Calcium sulfate occurs in nature in several different forms, the most common of which is *gypsum* ($CaSO_4 \cdot 2\,H_2O$). This is quarried in large amounts in New York, Michigan, and Oklahoma. It is used as a filler in making paper (p. 227), as a constituent of fertilizers, and especially in making *plaster of Paris.* It is but slightly soluble in water.

Plaster of Paris ($(CaSO_4)_2 \cdot H_2O$). This is a fine white powder obtained by carefully heating gypsum. When water is added to the powder, a plastic mass is formed which quickly hardens, or *sets.* This property makes it valuable for molding casts, for stucco work, and for a finishing coat on plastered walls. Broken bones are often held in place by casts of plaster of Paris until they grow together.

Calcium carbide (CaC_2). This compound is prepared on a large scale for use in the manufacture of acetylene (p. 207) and in making fertilizers. It is made by heating a mixture of lime and coke in an electric furnace:

$$CaO + 3\,C \longrightarrow CaC_2 + CO$$

The pure carbide is a colorless, transparent solid. The commercial article is a dull-gray porous substance which contains many impurities. It is placed on the market in air-tight containers.

Commercial preparation. While calcium carbide was first prepared in 1836, it was not until 1893 that it became a commercial product. The general principles involved in its preparation are illustrated in Fig. 152, which represents a simple type of a carbide furnace. The base of the furnace is provided with a large block of carbon *A*, which serves as one of the electrodes. The other electrodes, *B*, *B*, several in number, are arranged horizontally at some distance above this. A mixture of coal and lime is fed into the furnace through the trap top *C*, and in the lower part of the furnace this mixture becomes intensely heated, forming liquid carbide. This is drawn off through the tap hole *D*.

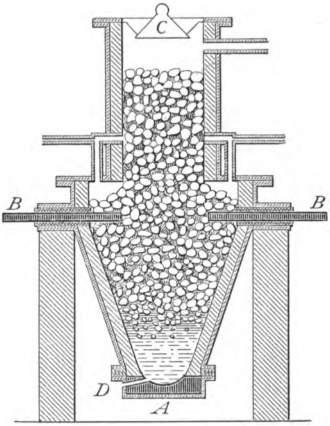


FIG. 152. A furnace for the manufacture of calcium carbide

Calcium cyanamide (CaN_2C). When nitrogen is passed over hot calcium carbide, the two react, forming a compound known as calcium cyanamide:

$$CaC_2 + N_2 \longrightarrow CaN_2C + C$$

The commercial product is impure, containing carbon, lime, besides about 60 per cent of the cyanamide. This product is known as *lime-nitrogen.* This is ground, mixed with water (which slakes the lime), and in this form sold as a fertilizer under the name *cyanamide.* Its value as a fertilizer lies in the fact that all of its nitrogen is available as a plant food.

The nitrogen used in the preparation of cyanamide is obtained by passing air (freed from moisture and carbon dioxide) over hot copper (p. 81). By means of this compound, therefore, it becomes possible to utilize the nitrogen in the air as a plant food (p. 83).

Calcium phosphate ($Ca_3(PO_4)_2$). This important substance occurs in nature as the mineral *phosphorite* and as a constituent of *apatite.* Large amounts of it occur in the form of *rock phosphate,* which is found especially in Florida, Tennessee, and some of the Western states. It is also the chief mineral constituent of bones. Bone ash is, therefore, nearly pure calcium phosphate.

Other compounds of calcium. *Calcium chloride* ($CaCl_2$) occurs in sea water and is formed in large quantities as a by-product in the Solvay process for making sodium carbonate. The anhydrous salt readily absorbs moisture and is used as an agent for drying gases. A solution of the salt is used as a brine in the manufacture of ice (p. 124). It has also been used to lay the dust on roads, and mines have been sprinkled with it in the hope of preventing dust explosions. *Calcium fluoride* (CaF_2) occurs in nature in the form of *fluorite.* It is mined in large quantities, especially in Illinois, and is used in the preparation of hydrofluoric acid, in the manufacture of opaque glass, and in various metallurgical operations. *Calcium sulfide* (CaS) is a by-product in the Leblanc process for making sodium carbonate. The commercial salt is sometimes used as a luminous paint, since, after exposure to a bright light, it will glow in the dark. *Calcium acid sulfite* ($Ca(HSO_3)_2$) is used as a preservative, and in large quantities in the manufacture of paper (p. 227). A number of *calcium silicates* are known, and derive their chief interest from the fact that they are important constituents of cement and glass.

STRONTIUM AND BARIUM

General. These elements are much rarer than calcium, are difficult to prepare, and have no commercial uses. Their compounds resemble those of calcium in composition and properties. Strontium compounds, especially the nitrate, when ignited with oxidizable substances, give a brilliant crimson color, and on this account are used in the manufacture of red lights. Under similar conditions barium nitrate gives a green light. The following compounds of barium are of importance.

Oxides of barium. Barium oxide (BaO) can be obtained by strongly heating the nitrate:

$$2\,Ba(NO_3)_2 \longrightarrow 2\,BaO + 4\,NO_2 + O_2$$

Heated to a low red heat in the air, the oxide combines with oxygen, forming the peroxide (BaO_2), which is used in making hydrogen peroxide (p. 52).

Barium chloride ($BaCl_2 \cdot 2\,H_2O$). Barium chloride is a white solid. It is used in the laboratory as a reagent to detect the presence of sulfuric acid or soluble sulfates, reacting with these to form the insoluble barium sulfate.

Barium sulfate (barite) ($BaSO_4$). Barium sulfate occurs in nature as a heavy white mineral known as *barite.* It is precipitated as a crystalline powder when a barium salt is added to a solution of a sulfate or to sulfuric acid:

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\,HCl$$

It is used in large quantities in the manufacture of paints.

EXERCISES

1. What properties have the alkaline earth metals in common with the alkali metals? In what respect do they differ?

2. Write the equation for the reaction between calcium carbide and water.

3. How is calcium chloride removed from hard water?

4. Would air-slaked lime do for making mortar? Would it serve for liming acid soils (p. 110)?

5. Why would you expect calcium carbide to contain impurities?

6. How do you explain the fact that calcium carbonate can be decomposed into calcium oxide and carbon dioxide, and yet calcium oxide absorbs carbon dioxide from the air to form the carbonate?

7. Could barium hydroxide be used in place of calcium hydroxide in testing for carbon dioxide?

8. Calcite and gypsum often resemble each other in appearance. How could you easily distinguish between the two?

9. What weight of plaster of Paris can be made by heating 1 ton of gypsum? *Ans.* 1686 lb.

10. What weight of limestone is necessary to prepare 10 tons of lime? *Ans.* 39,262 lb.

11. What weight of water is necessary to slake 1 ton of lime? *Ans.* 642 lb.

12. How could you prove that dried mortar contains calcium carbonate and sand?

TOPICS FOR THEMES

If possible, inspect a limekiln and write a description of the process.

The great caves of the United States (see encyclopedia).

Find out whether any of the factories in your vicinity soften the water used in their boilers, and if they do, write a description of the process.

CHAPTER XXXII

FERTILIZERS

Plant food; fertilizers. With the exception of carbon dioxide (and possibly a little oxygen) absorbed from the air, the growing plant derives its nourishment from the soil. In order that vegetation may thrive, it is essential, therefore, that the soil should contain an adequate supply of appropriate plant food. Moreover, since this supply is continually being drawn upon by the growing plant, it is necessary, in order that the soil may retain its fertility, that the ingredients so withdrawn shall be returned to it. It is for this purpose that fertilizers are used.

Constituents of fertilizers. While a number of elements are essential to the growth of the plant, experience has shown that in general the fertility of the soil may be maintained by adding three substances: (1) nitrogenous matter, (2) phosphates of calcium, and (3) compounds of potassium.

Sources of fertilizers. The commercial sources of each of the constituents of fertilizers are as follows:

1. ***Nitrogenous matter.*** This is obtained from a number of sources: sodium nitrate, ammonium sulfate, and cyanamide; also nitrogenous organic matter, such as dried blood, the waste from slaughterhouses, and, especially, animal excrements.

2. ***Phosphates.*** Ground bones are especially valuable, since they contain some nitrogen in addition to calcium phosphate. This source, however, is entirely inadequate, and the great supply comes from the rock phosphates,

which contain about 70 per cent calcium phosphate. These rock phosphates are quarried in large quantities, especially in Florida (Fig. 153) and Tennessee. Since calcium phosphate is nearly insoluble, the rock is ground and then treated with sulfuric acid. This converts the insoluble calcium phosphate into the soluble calcium acid phosphate ($CaH_4(PO_4)_2$):

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \longrightarrow 2\,CaSO_4 + CaH_4(PO_4)_2$$

The calcium sulfate also adds to the value of the fertilizer, furnishing sulfur and improving the physical qualities of the soil. Certain products (slags) formed in the manufacture of steel contain phosphorus, and are also used in fertilizers.

FIG. 153. Mining phosphate rock in Florida

3. ***Potassium compounds.*** These are obtained from the Stassfurt mines. Kainite ($KCl \cdot MgSO_4 \cdot 3\,H_2O$) is the most common of the minerals used (p. 286). Wood ashes are excellent, but the supply is limited.

Commercial fertilizers. As a rule the fertilizers on the market are mixtures of the three fundamental materials referred to above. The composition is varied according to the crop to be grown as well as to the nature of the soil; for example, potatoes demand a fertilizer rich in potassium, while a cereal, such as wheat, is benefited more by one rich in phosphates. Instead of using a fertilizer containing all three constituents, many farmers prefer to find out by experiment just what plant food is lacking in their soils and then to make a proper mixture of such fertilizing materials as will furnish the desired food. Fig. 154 shows the result of such an experiment. Pot 1 shows the result obtained with no fertilizer; pot 2, with one combination; and pot 3, with another.

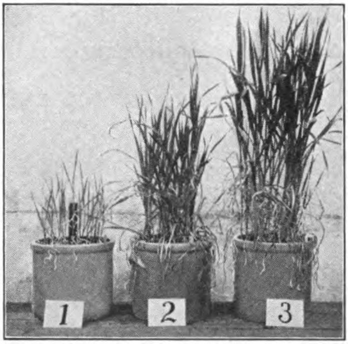


FIG. 154. The effect of fertilizers upon the growth of plants

The liming of soils. Sometimes a soil may be unproductive from other causes than deficiency in plant food. For example, it may be acid in reaction, and in such a case it may be made fertile once more by being *limed* (p. 110).

The utilization of atmospheric nitrogen. It has been pointed out that with few exceptions plants have not the power of assimilating free nitrogen (p. 83). Moreover, it is inevitable that the supplies of sodium nitrate and ammonium sulfate, which are now the chief nitrogenous products used in the manufacture of commercial fertilizers, will sooner or later become exhausted. Repeated efforts have therefore been made to utilize the inexhaustible supply of nitrogen in the atmosphere. It has been found possible to do this by converting the nitrogen into compounds which contain the element in a form available for plant food.

The following methods may be used for effecting this change: (1) the nitrogen may be converted into cyanamide (p. 305); (2) the nitrogen may be converted into nitric acid by electric sparking, and then into nitrates (p. 128); (3) ammonia may be formed by heating a mixture of nitrogen and hydrogen (p. 123), and this, with sulfuric acid, gives ammonium sulfate. These methods are now used commercially to a limited extent, and it appears certain that before long the quantity of nitrogenous compounds annually required for fertilizers will be prepared from atmospheric nitrogen.

EXERCISES

1. If the crops grown on a soil were not removed, would the soil diminish in fertility? Would it increase in fertility?

2. Why does treatment of bones with sulfuric acid make them more available as plant food?

3. In the preparation of fertilizers, what weight of sulfuric acid containing 50 per cent hydrogen sulfate is necessary in the treatment of 10 tons of rock phosphate containing 70 per cent pure calcium phosphate? *Ans.* 17,702 lb.

TOPIC FOR THEMES

The utilization (fixation) of atmospheric nitrogen (Duncan, Chemistry of Commerce).

CHAPTER XXXIII

THE MAGNESIUM FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	BOILING POINT	OXIDE
Magnesium	Mg	24.32	1.74	651°	920°	MgO
Zinc . . .	Zn	65.37	7.10	419.4°	950°	ZnO
Cadmium .	Cd	112.4	8.64	320.9°	778°	CdO

The family. In the magnesium family are included the four elements: magnesium, zinc, cadmium, and mercury. Between the first three of these metals there is a close family resemblance. Mercury in some respects is more similar to copper and will be studied in connection with that metal.

MAGNESIUM

Occurrence. Magnesium is a very abundant element in nature, ranking a little below calcium in this respect. Like calcium, it is a constituent of many rocks and also occurs in the form of soluble salts. It is a constituent of *chlorophyll* and is therefore essential to plant life.

Preparation. The metal magnesium, like most metals whose oxides are difficult to reduce with carbon, is made by electrolysis; but instead of using as the electrolyte the melted anhydrous chloride, which is difficult to obtain, the mineral *carnallite* (p. 286) is used. This is melted in an iron pot which also serves as the cathode in the electrolysis.

A rod of carbon dipping into the melted salt serves as the anode. The apparatus is very similar to those employed in the preparation of sodium and calcium.

Properties. Magnesium is a silvery-white metal of small density. It is usually sold in the form of thin ribbon or of wire or as a powder. Air does not act rapidly upon it, but a thin film of basic carbonate forms upon its surface, dimming its bright luster. The common acids dissolve it with the formation of the corresponding salts. It can be ignited readily, and in burning it gives a brilliant white light. This light is very rich in the rays which affect photographic plates, and the metal, in the form of fine powder, is extensively used in the production of *flash lights* and for white lights in pyrotechnic displays. When used for this purpose, the powder is mixed with an oxidizing agent, potassium chlorate being the one commonly employed.

Magnesium oxide (magnesia) (MgO). Magnesium oxide, sometimes called *magnesia* or *magnesia usta*, resembles lime in many respects. It is much more easily formed than lime and can be made in the same way, namely, by heating the carbonate. It is a white powder, very soft and bulky, and is unchanged by heat even at very high temperatures. For this reason it is used in the manufacture of crucibles, for lining furnaces, and for other purposes where a refractory basic substance is needed.

Magnesium hydroxide ($Mg(OH)_2$). The hydroxide of magnesium is but slightly soluble in water and can be precipitated by adding a soluble base to a salt of magnesium:

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$$

It dissolves sufficiently to give a slightly alkaline reaction, and is a moderately strong base. It is a white amorphous substance, and is converted into the oxide when heated.

Magnesium carbonate ($MgCO_3$). Magnesium carbonate occurs in a number of localities as *magnesite*, which is usually amorphous, but sometimes forms pure crystals resembling calcite. More frequently it is found associated with calcium carbonate. The mineral *dolomite* has the composition $CaCO_3 \cdot MgCO_3$. Limestone containing smaller amounts of magnesium carbonate is known as *dolomitic limestone*. Dolomite is one of the most common rocks, forming whole mountain masses. It is harder and less readily attacked by acids than limestone. It is valuable as a building-stone and for foundations and as ballast for roadbeds. Like calcium carbonate, magnesium carbonate is insoluble in water, but readily dissolves in water containing carbon dioxide, forming the acid carbonate:

$$MgCO_3 + H_2O + CO_2 \longrightarrow Mg(HCO_3)_2$$

Boiler scale. When water which contains certain salts in solution is evaporated in steam boilers, a hard, insoluble material called *scale* deposits in the boiler. The formation of this scale may be due to several distinct causes:

1. ***To the deposit of calcium sulfate.*** This salt, while sparingly soluble in cold water, is almost completely insoluble in superheated water. Consequently it is precipitated when water containing it is heated in a boiler.

2. ***To decomposition of acid carbonates.*** As we have seen, calcium and magnesium acid carbonates are decomposed on heating, forming insoluble normal carbonates:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

3. ***To hydrolysis of magnesium salts.*** Magnesium chloride, and to some extent magnesium sulfate, undergo hydrolysis when superheated in solution, and the magnesium hydroxide, being sparingly soluble, precipitates:

$$MgCl_2 + 2\,H_2O \longrightarrow Mg(OH)_2 + 2\,HCl$$

This scale adheres tightly to the boiler tubes in compact layers (Fig. 155), and, being a nonconductor of heat, causes much waste of fuel. It is very difficult to remove, owing to its hardness and its resistance to reagents. Thick scale sometimes cracks, and the water coming in contact with the overheated iron occasions an explosion.

Magnesium sulfate ($MgSO_4$). Like the chloride, magnesium sulfate is found rather abundantly in springs and in salt deposits. Deposits of the almost pure solid salt having the composition $MgSO_4 \cdot 7H_2O$ have been found in Wyoming and Washington. It is often called Epsom salt because of its occurrence in the waters of the Epsom springs in England.

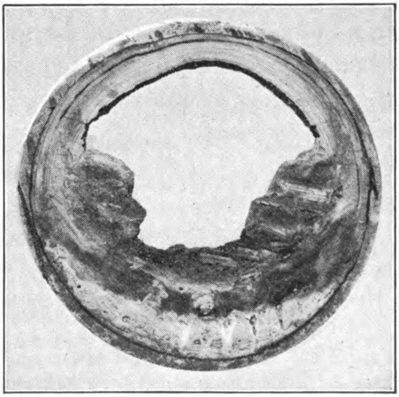


FIG. 155. Cross section of a boiler tube showing the deposit of boiler scale

Magnesium sulfate is used to a small extent in the preparation of sodium and potassium sulfates; for weighting cotton cloth in the dye industry; in tanning; and in the manufacture of paints and laundry soaps. To some extent it is used in medicine.

Magnesium silicates. Many silicates containing magnesium are known, and some of them are important substances. *Serpentine*, *asbestos*, *talc* (or *soapstone*), and *meerschaum* are examples of such substances. Asbestos is soft and fibrous and a nonconductor of heat. It is used for fireproof material in a great variety of forms, such as cloth, paper, board, and rope. It is also used as a covering for pipes, furnaces, and boilers, to diminish heat radiation. Soapstone is valuable for sinks and table tops, and in finely ground form as a toilet powder and foot ease, and is called *French chalk.* Meerschaum is used for pipe bowls and similar articles.

ZINC

Occurrence. Zinc never occurs free in nature. It is not a constituent of common rocks and minerals, and its occurrence is rather local and confined to definite deposits or to pockets. It occurs chiefly in the following ores: sphalerite (zinc blende) (ZnS); zincite (ZnO); smithsonite ($ZnCO_3$); franklinite ($ZnO \cdot Fe_2O_3$). One fourth of the world's output of zinc comes from the United States—Missouri, Kansas, and New Jersey being the largest producers.

Metallurgy. The ores employed in the preparation of zinc are chiefly the sulfide, oxide, and carbonate. They are first heated in the air, by which process they are changed into the oxide, this process being called *roasting*:

$$ZnCO_3 \longrightarrow ZnO + CO_2$$
$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$

The oxide is then mixed with coal dust, and the mixture is heated in earthenware retorts. The oxide is reduced by this means to the metallic state, and the zinc, being heated above its boiling point, distills and is collected in suitable receivers and is drawn off into molds. In this form it is called *spelter.* Commercial zinc often contains a number of impurities, especially carbon, arsenic, and iron.

Properties. Pure zinc is a rather heavy bluish-white metal with a high luster. It melts at about 420°, and if heated much above this temperature in the air, it takes fire and burns with a bluish flame. It boils at about 950°.

Many of the properties of zinc are much influenced by the temperature and previous treatment of the metal. When cast into ingots from the liquid state, it becomes at ordinary temperatures quite hard, brittle, and highly crystalline. At 100°–150° it is malleable and can be rolled into thin sheets; at higher temperatures it again becomes very brittle. When once rolled into sheets it retains its softness and malleability at ordinary temperatures. When melted and poured into water it forms thin, brittle flakes, and in this condition is called *granulated zinc* or *mossy zinc.*

Zinc is tarnished superficially by moist air, but beyond this is not affected by it. When the metal is quite pure, sulfuric and hydrochloric acids act upon it very slowly; when, however, it contains small amounts of other metals, such as magnesium or copper, or when it is merely in contact with another metal, brisk action takes place and hydrogen is evolved. For this reason, when pure zinc is used in the preparation of hydrogen, a few drops of copper sulfate are often added to the solution to assist the chemical action.

Uses of zinc. The chief use of zinc is in the manufacture of galvanized iron. This is sheet iron or wire covered with a thin layer of zinc, which protects the iron from rusting. About two thirds of all the zinc produced is used in this way. Sheet zinc is used as a lining for sinks and water-containers. Large quantities of the metal are used in making brass and other alloys (p. 360), in the construction of electrical batteries, and in separating silver from lead (p. 373). In the laboratory it is used in the preparation of hydrogen and, in the form of zinc dust, as a reducing agent.

Manufacture of galvanized iron. Fig. 156 shows the method used in making galvanized iron. The plates of iron pass under the rollers at *A* and on into the pot of melted zinc *B*. The zinc adheres to the iron, and the resulting plate is passed under the roller *C* to remove the excess of zinc and to render the surface smooth. Sometimes the zinc is deposited on the iron by electrolytic methods.

Zinc oxide (zinc white) (ZnO). Zinc oxide occurs in impure form in nature, being colored red by manganese and iron compounds. It can be prepared in the same way as magnesium oxide, namely, by heating zinc carbonate or hydroxide, but is more often made by burning the metal.

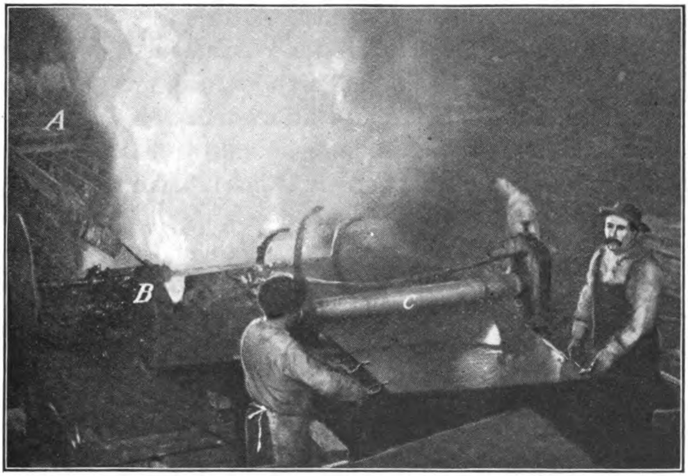


FIG. 156. The manufacture of galvanized sheet iron

Zinc oxide is a pure-white powder which is much used as a white pigment in paints, under the name of *zinc white.* It has an advantage over white lead in that it is not changed in color by sulfur compounds, while lead compounds turn black. Many thousand tons of zinc oxide are used in paints each year. It is also used as a filler in the manufacture of rubber goods. More than two thousand tons are used annually in the manufacture of automobile tires.

Zinc sulfate ($ZnSO_4$). This salt is readily crystallized from concentrated solutions in transparent colorless crystals which have the formula $ZnSO_4 \cdot 7\,H_2O$ and are called *white vitriol.* It is prepared commercially by careful roasting of the sulfide:

$$ZnS + 2\,O_2 \longrightarrow ZnSO_4$$

Zinc chloride ($ZnCl_2$). This salt is very soluble in water and has a strongly acid reaction. It has germicidal properties and is used to preserve railroad ties and other wooden timbers especially subject to decay.

Zinc sulfide (ZnS). This substance occurs as the mineral *sphalerite,* and is one of the most valued ores of zinc. Very large deposits occur in southwestern Missouri. The natural mineral is found in large crystals or masses, resembling resin in color and luster. It is insoluble in water and, when prepared by precipitation, is white. *Lithopone* is a mixture of the two solids, barium sulfate and zinc sulfide, made by bringing together barium sulfide and zinc sulfate in solution:

$$BaS + ZnSO_4 \longrightarrow BaSO_4 + ZnS$$

It is a valuable white-paint pigment.

Preservation of wood. With the rapid disappearance of the forests the preservation of wood from decay (fungous growths) becomes a very important problem. When the wood is to be exposed merely to atmospheric conditions, it is preserved by paints and varnishes. When it must be partly buried in the ground (railway ties, fence posts), it is treated with germicidal preservatives. Those most frequently used are zinc chloride, copper sulfate, and creosote.

The wood is placed in closed boilers in baths of the appropriate liquid, and the air is exhausted so that the liquid may be more readily driven into the pores of the wood. Frequently the latter process is assisted by the application of considerable pressure to the liquid after the air has been pumped out.

Cadmium. This element very closely resembles zinc in most respects. Some of its alloys are characterized by having low melting points. Its compounds are similar in composition to the corresponding ones of magnesium and zinc.

EXERCISES

1. What metals already studied are prepared by electrolysis?

2. When acids act upon magnesium, is hydrogen liberated?

3. What property of magnesium was taken advantage of in the isolation of argon?

4. How could you distinguish between Glauber's salt and Epsom salt?

5. Account for the fact that paints made of zinc oxide are not colored by hydrogen sulfide.

6. Why does not zinc occur in the uncombined state in nature?

7. What reaction takes place when zinc is added to a solution of copper sulfate? (See displacement series.)

8. Write equations showing how the following compounds of zinc may be obtained from metallic zinc: the oxide, chloride, nitrate, carbonate, sulfate, sulfide, hydroxide.

9. What is the composition of a lime made from dolomite?

10. Which would yield the most zinc, 1 ton of sphalerite or 1 ton of franklinite?

TOPICS FOR THEMES

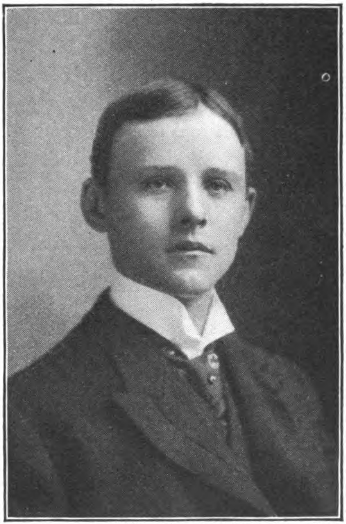
The zinc mines of Missouri (United States Geological Survey, Washington).

The galvanizing of iron (see encyclopedia).

CHAPTER XXXIV

ALUMINIUM

Occurrence. Aluminium never occurs in the free state in nature, owing to its great affinity for oxygen. In combined form, as oxide, silicates, and a few other compounds, it is both abundant and widely distributed, being an essential constituent of all soils, and of most rocks except limestone and sandstone. It is estimated that aluminium constitutes about 8 per cent of the earth's crust. *Cryolite* (Na_3AlF_6), found in Greenland, and *bauxite*, which is an aluminium hydroxide usually mixed with some iron hydroxide, are important minerals. In the industries the metal is called *aluminum*, but its chemical name is *aluminium*.



Courtesy of The Chemists' Club, New York

FIG. 157. Charles Martin Hall (1863–1914)

The American chemist who developed the electrical method for producing aluminium

Preparation. Aluminium was first prepared by Wöhler, in 1827, by heating anhydrous aluminium chloride with potassium:

$$AlCl_3 + 3\,K \longrightarrow 3\,KCl + Al$$

Although the metal is very abundant in nature and possesses many desirable properties, the cost of separating it from its ores was so great that it remained almost a curiosity until comparatively recent years. With the development of cheap ways of obtaining electrical energy the problem has been solved, and the metal is now produced by the electrolysis of aluminium oxide (Al_2O_3) dissolved in melted cryolite —a method devised by the American chemist Hall (Fig. 157) in 1886. The annual production of aluminium now exceeds 50,000,000 lb. During the last twenty-five years its cost has decreased from $5 to 20 cents per pound.

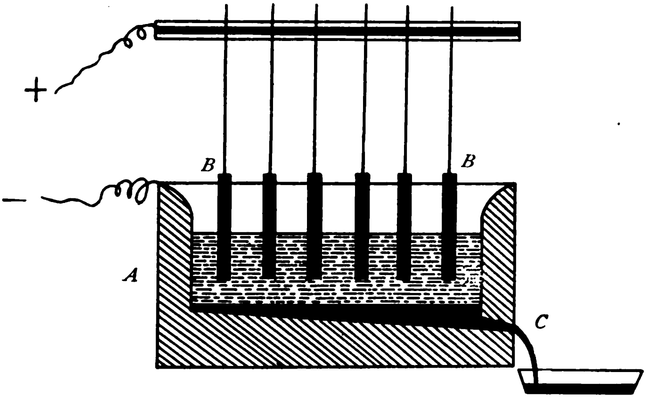


FIG. 158. Diagram illustrating the manufacture of aluminium

Metallurgy. An iron box *A* (Fig. 158) about 8 ft. long and 6 ft. wide is connected with a powerful electrical generator in such a way as to serve as the cathode upon which the aluminium is deposited. Three or four rows of carbon rods *B*, *B* dip into the box and serve as the anodes. The box is partly filled with cryolite, and the current is turned on, generating enough heat to melt the cryolite. Aluminium oxide is then added, and acts as an electrolyte, being decomposed into aluminium and oxygen.

The temperature is maintained above the melting point of aluminium, and the liquid metal, being heavier than cryolite, sinks to the bottom of the vessel, from which it is tapped off from time to time through the tap hole *C*.

Properties. Aluminium is a tin-white metal which melts at 658.7° and is very light, its density being about one third that of iron. It is stiff and strong, and with frequent heating can be rolled into thin foil. It is a good conductor of heat and electricity, though not so good as copper *for a given cross section of wire.*

Aluminium is not perceptibly acted on by boiling water, and moist air merely dims its luster. Further action is prevented in each case by the formation of an extremely thin film of oxide upon the surface of the metal. When heated in oxygen it burns with great energy and with the liberation of much heat. It is therefore a good reducing agent. Hydrochloric acid acts upon it, forming aluminium chloride; nitric acid and dilute sulfuric acid have almost no action on it; but hot concentrated sulfuric acid acts upon it in the same way as upon copper, forming aluminium sulfate. Alkalies readily attack it, liberating hydrogen:

$$2\,Al + 6\,KOH \longrightarrow 2\,Al(OK)_3 + 3\,H_2$$

Salt solutions, such as sea water, corrode the metal rapidly.

Uses of aluminium. These properties suggest many uses for the metal. Its lightness, strength, and inactivity toward air and water make it well adapted for many construction and manufacturing purposes. These same properties have led to its extensive use in the manufacture of cooking utensils. Owing to its small resistance to electrical currents, it is replacing copper to some extent in electrical construction, especially for trolley and power wires. In the form of a powder suspended in a suitable liquid it makes a silvery paint used to cover iron pipes and lantern curtains. The greatest use of aluminium is in the steel industry (p. 348). Aluminium bronze, consisting of about 90 per cent copper and 10 per cent aluminium, has a pure-golden color, is strong and malleable, is easily cast, and is permanent in the air. Magnalium is an alloy of aluminium and magnesium. It is light and rigid and is used for balance beams.

Goldschmidt reduction process. Aluminium is frequently employed as a powerful reducing agent, many metallic oxides which resist reduction by carbon being readily reduced by it. The aluminium, in the form of a fine powder, is mixed with the metallic oxide, together with some substance such as fluorite to act as a flux. The mixture is ignited, and the aluminium unites with the oxygen of the metallic oxide, liberating the metal. This collects in a fused condition under the melted fluorite.

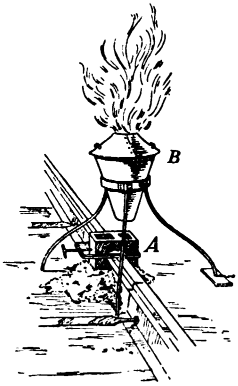


FIG. 159. Welding a rail with thermite

Thermite welding process. The property possessed by aluminium of reducing oxides with the liberation of a large amount of heat is turned into practical account in the welding of metals. The German chemist Goldschmidt was the first to use aluminium for this purpose. The welding of metals by this method may be illustrated by a single example, namely, the welding of car rails — a process often carried out in connection with electric railways to secure good electrical connection. The ends of the rails are accurately aligned and thoroughly cleaned. A sand mold *A* (Fig. 159) is then clamped about the ends of the rail, leaving sufficient space so that the metal can flow in. The ends of the rails are heated to redness by the flame from a gasoline compressed-air torch directed into the opening in the mold. Just over the opening is placed the conical-shaped crucible *B*, which contains a mixture of iron, metallic oxides, and aluminium. When the ends of the rails have been heated to redness by the torch, the mixture in the crucible is ignited, and after a few seconds the crucible is opened at the bottom, and the molten metal resulting from the reaction in the crucible is allowed to flow into the mold. In this way the molten metal surrounds the ends of the rails and, as it cools, welds them firmly together. A mixture of the metallic oxides and aluminium ready for use in welding is sold under the name of *thermite.*

Aluminium oxide (Al_2O_3). This substance occurs in several forms in nature. The relatively pure crystals are called *corundum*; *emery* is a variety colored dark gray or black, usually by iron compounds. In transparent crystals, tinted different colors by traces of impurities, it forms such precious stones as the *sapphire*, *ruby*, *topaz*, and *oriental amethyst.* All these varieties are very hard, falling little short of the diamond in this respect. The cheaper forms, corundum and emery, are used for cutting and grinding purposes. Chemically pure aluminium oxide can be made by igniting the hydroxide, when it forms a white powder:

$$2\,Al(OH)_3 \longrightarrow Al_2O_3 + 3\,H_2O$$

The artificially prepared oxide is largely used in the preparation of aluminium. Some laboratory utensils such as crucibles and tubes are made of aluminium oxide, which is given the trade name *Alundum.* The same material is used for cutting and polishing metals.

Artificial gems. A number of gems are now prepared in the laboratory from molten aluminium oxide. The white sapphires so extensively advertised are simply the pure oxide. By incorporating with the melted oxide small percentages of certain metallic oxides, different tints or colors are obtained, and in this way are prepared such gems as the ruby, the oriental amethyst, and the yellow and blue sapphires, which are practically identical in composition and properties with the natural stones.

Aluminium hydroxide ($Al(OH)_3$). The hydroxide can be prepared by adding ammonium hydroxide to any soluble aluminium salt, forming a colloidal precipitate which is insoluble in water but very hard to filter. When heated, it is decomposed, forming the oxide and water. It dissolves in most acids to form soluble salts, and in the strong bases to form aluminates, as indicated in the equations

$$Al(OH)_3 + 3\,HCl \longrightarrow AlCl_3 + 3\,H_2O$$
$$Al(OH)_3 + 3\,NaOH \longrightarrow Al(ONa)_3 + 3\,H_2O$$

It may act, therefore, either as a weak base or as a weak acid, its action depending upon the character of the substances with which it is in contact.

Water purification. The value of aluminium hydroxide in the purification of water (p. 44) is due largely to its colloidal or gelatinous character when freshly formed by precipitation. After being stirred through the water it is allowed to slowly settle, and in so doing it carries with it any suspended matter present, including microörganisms and coloring materials. Instead of adding aluminium hydroxide itself to the water, it is more economical and effective to produce it by precipitation. This is done by dissolving in the water some cheap salt which readily hydrolyzes, such as aluminium sulfate:

$$Al_2(SO_4)_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3 + 3\,H_2SO_4$$

There is always sufficient basic material present in the water to combine with the sulfuric acid set free, so that no acid is left in the water as a result of this treatment.

Fig. 160 illustrates the use of aluminium sulfate in purifying water. The cylinder *A* contains impure water. *B* is a similar cylinder of water to which some aluminium sulfate has been added. The aluminium hydroxide formed by hydrolysis is slowly settling in the water, carrying with it the impurities. The appearance of the water after settling is shown in *C*.

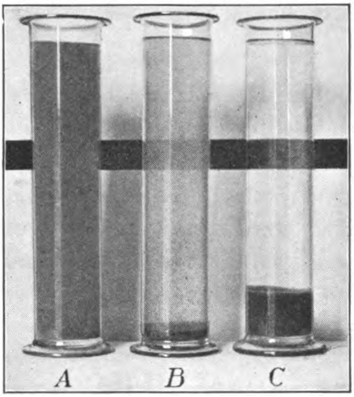


FIG. 160. Purification of water by aluminium sulfate

Alums. Aluminium sulfate can be prepared by the action of sulfuric acid upon the mineral bauxite. It has the property of combining with the sulfates of the alkali metals to form compounds called *alums*. Thus, with potassium sulfate the reaction is expressed by the equation

$$K_2SO_4 + Al_2(SO_4)_3 + 24\,H_2O \longrightarrow 2\,(KAl(SO_4)_2 \cdot 12\,H_2O)$$

The sulfates of other trivalent metals can form similar compounds with the alkali sulfates, and these compounds are also called alums, though they contain no aluminium. They all crystallize in octahedra and contain 12 molecules of water of hydration. The alums most frequently prepared are the following:

Potassium alum	$KAl(SO_4)_2 \cdot 12\,H_2O$
Ammonium alum	$NH_4Al(SO_4)_2 \cdot 12\,H_2O$
Ammonium iron alum	$NH_4Fe(SO_4)_2 \cdot 12\,H_2O$
Potassium chrome alum	$KCr(SO_4)_2 \cdot 12\,H_2O$

Very large, well-formed crystals of an alum can be prepared by suspending a small crystal by a thread in a saturated solution of the alum, as shown in Fig. 161. The small crystal slowly grows and assumes a very perfect form.

Hydrolysis of salts of aluminium. While aluminium hydroxide forms fairly stable salts with strong acids, it is such a weak base that its salts with weak acids are readily hydrolyzed (p. 138). Thus, when an aluminium salt and a soluble carbonate are brought together in solution, we should expect to have aluminium carbonate precipitated according to the equation

$$3\,Na_2CO_3 + 2\,AlCl_3 \longrightarrow Al_2(CO_3)_3 + 6\,NaCl$$

But if it is formed at all, it instantly begins to hydrolyze, the products of the hydrolysis being aluminium hydroxide and carbonic acid:

$$Al_2(CO_3)_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3 + 3\,H_2CO_3$$

Aërating agents used in baking. In preparing foods made largely from dough, such as bread, biscuits, and cake, it is essential that some *aërating agent* be used to render the food light and wholesome. The aërating agent used in all cases is carbon dioxide. This is generated in the dough and, pushing its way through the mass, renders it porous and light. The following methods are used for generating the gas in baking:

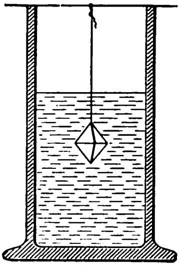


FIG. 161. The formation of a crystal of alum

1. **By alcoholic fermentation.** As we have seen, this is the method generally used in making bread (p. 231).

2. **By the action of sour milk on sodium bicarbonate.** The lactic acid present in the sour milk (p. 222) slowly acts upon the bicarbonate, liberating carbon dioxide:

$$H \cdot C_3H_5O_3 + NaHCO_3 \longrightarrow NaC_3H_5O_3 + H_2O + CO_2$$

This method has largely been replaced by the following one:

3. **By the action of an acid salt or alum upon sodium bicarbonate; baking powders.** Mixtures of sodium bicarbonate, flour (or starch), and some substance that will act upon the bicarbonate to liberate carbon dioxide are known as *baking powders.* The compounds commonly employed for liberating the carbon dioxide are either alum, cream of tartar (potassium bitartrate) (p. 237), or calcium acid phosphate, and baking powders are known as *alum baking powders, cream of tartar baking powders,* or *phosphate baking powders,* according to whether they contain the one or other of these constituents. The reactions take place only in the presence of water; hence the use of the flour, which, by absorbing any moisture that may be present, prevents the powder from losing its strength until used. In place of alum a mixture of sodium sulfate and aluminium sulfate known as cream of tartar substitute, or simply as C. T. S., is now being largely used. Alum baking powders are much cheaper than those made from cream of tartar.

The reactions of baking powders. The reactions that take place when water is added to each of the classes of baking powders are represented in the following equations:

Alum (supposing that the alum present is potassium alum):

$$2\,KAl(SO_4)_2 + 6\,NaHCO_3 \longrightarrow 2\,Al(OH)_3 + 3\,Na_2SO_4 + K_2SO_4 + 6\,CO_2$$

Cream of tartar:

$$KHC_4H_4O_6 + NaHCO_3 \longrightarrow KNaC_4H_4O_6 + H_2O + CO_2$$

Phosphate:

$$CaH_4(PO_4)_2 + 2\,NaHCO_3 \longrightarrow CaHPO_4 + Na_2HPO_4 + 2\,H_2O + 2\,CO_2$$

Dyes and dyeing. To gain an understanding of the art of dyeing it is necessary to keep in mind (1) the characteristics that a good dye must have, and (2) the process of fastening the dye upon the fabric.

1. ***The dyes.*** The requisites of a good dye are as follows: (*a*) it must have an acceptable color; (*b*) it must not injure the fibers; (*c*) it must *dye fast*; in other words, the cloth after having been dyed must retain its color when washed with water; (*d*) it must not fade too easily. In olden times nearly all the dyes used were extracted from plants and trees. These dyes give rather dull but pleasing colors, and the beautiful tones of oriental rugs and tapestries are primarily due to their use. In 1856 the Englishman, W. H. Perkin, then but eighteen years of age, prepared the first aniline dye. The preparation of others soon followed, until to-day thousands of these dyes are manufactured, of every variety of color, while new ones are constantly being added to the list. Moreover, two of our most common dyes, indigo and alizarin, which were formerly obtained from vegetable sources, are now manufactured (p. 232) from coal-tar hydrocarbons. These aniline dyes (or coal-tar dyes) have a much higher coloring power than the vegetable dyes, and have almost entirely superseded them. They are all very complex compounds.

2. ***The process of dyeing.*** This process consists in fixing the dye uniformly upon the fabric. The animal fibers, namely, wool and silk, are as a rule more readily dyed than cotton, which is a vegetable fiber. To dye wool and silk with most dyes it is only necessary to steep the fabric in a solution of the dye. Cotton fabrics, when treated in this way, will become colored, but as a rule the color is not *fast*. Cotton fabrics may be dyed fast in the following way:

The cloth is first soaked in a solution of an aluminium salt (or a similar substance), which readily undergoes hydrolysis. The cloth is then exposed to the action of steam, which decomposes the salt, leaving the hydroxide thoroughly incorporated in the fiber. The cloth is then steeped in the dye, which is absorbed by the aluminium hydroxide, and is in consequence fastened, or "fixed," upon the fiber. Aluminium hydroxide and other substances which act in the same way are called *mordants*. The same dye will often give different colors with different mordants.

Lakes. The compounds which serve well as mordants may be precipitated in solutions containing various dyes, and the precipitate will be highly colored, though not always of the same color as the dye. Colored precipitates of this kind are called *lakes* and are used as pigments in paints.

EXERCISES

1. Why should not aluminium be made by electrolyzing the melted hydroxide as with so many other metals?

2. What familiar articles can you mention which are now made of aluminium?

3. What is a colloidal substance?

4. Why do the directions for using aluminium cooking utensils state that such utensils must not be washed in strongly alkaline solutions?

5. What is the meaning of the word *mordant* (see dictionary)?

6. Calculate the weights of substances necessary for the preparation of 10 lb. of cream of tartar baking powder, supposing that such powders contain 25 per cent of starch. *Ans.* Starch, 40 oz.; bicarbonate of soda, 37 oz.; cream of tartar, 83 oz.

7. What volume of carbon dioxide measured at 200° would be evolved by 6 g. (approximately 2 level teaspoonfuls) of a baking powder of the composition found in problem 9? *Ans.* 849 cc.

8. It will be of interest to calculate the data in problems 6 and 7 for each of the other classes of baking powders and to compare the results.

TOPICS FOR THEMES

The dyeing of cloth (Lassar-Cohn, Chemistry in Daily Life).

The advantages of aluminium for cooking utensils. (Consult dealers.)

Artificial gems (Duncan, The Chemistry of Commerce).

CHAPTER XXXV

ALUMINIUM SILICATES AND THEIR COMMERCIAL APPLICATIONS

Aluminium silicates. One of the most common constituents of rocks is feldspar ($KAlSi_3O_8$), a mixed salt of potassium and aluminium with polysilicic acid ($H_4Si_8O_8$). Under the influence of moisture, carbon dioxide, and changes of temperature this substance is constantly being broken down into soluble potassium compounds and aluminium silicate ($Al_2Si_2O_7 \cdot 2\,H_2O$). In relatively pure condition it is called *kaolin* and is a soft, plastic mineral; in the impure state, mixed with sand and other substances, it forms common *clay*. *Mica* is another very abundant mineral, having a varying composition, but being essentially of the formula $KAlSiO_4$. *Serpentine*, *talc*, *asbestos*, and *meerschaum* are important complex silicates of aluminium and magnesium; *granite* is a mechanical mixture of quartz, feldspar, and mica and is therefore rich in aluminium. *Fuller's earth* is a peculiar form of aluminium silicate, which is used as a filtering material for decolorizing oils, especially cottonseed oil.

Clay products. The crudest forms of clay products, such as porous brick and draintile, have little chemistry involved in their manufacture. Natural clay is molded into the required form, dried, and then burned in a kiln, but not to a temperature at which the materials soften. In this process the nearly colorless iron compounds in the clay are converted into colored compounds which give the usual red color to these articles. In making *vitrified brick* the temperature is raised to the point at which fusion begins, so that the brick is partially changed to a kind of glass.

White pottery. This term is applied to a variety of articles varying from the crudest porcelain to the finest chinaware. While the processes used in the manufacture of the articles differ in details, fundamentally they are the same and may be described under three heads: namely, (1) the preparation of the body of the ware, (2) the process of glazing, and (3) the decoration.

1. **The body of the ware.** The materials used consist of an artificially compounded clay made from kaolin, plastic clay, and pulverized feldspar. This mixture is plastic and is worked into the desired shape by molds or on a potter's wheel (Fig. 162). The ware is then dried and burned in a kiln (Fig. 163) until vitrified, and in this form is known as *bisque*. This is usually porous and must therefore be glazed to render it nonabsorbent.

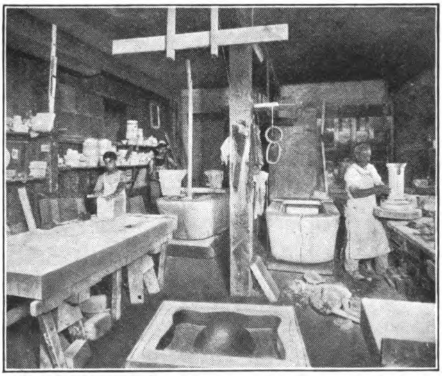


FIG. 162. The manufacture of pottery; molding the plastic material into form

2. **The glaze.** The glaze is a fusible glass which is melted over the surface of the body. The constituents of the glaze are quartz, feldspar, and various metallic oxides, often mixed with a little boric oxide. These materials are finely ground and mixed with water to a paste. Sometimes they are first fused into a glass, which is then powdered and made into the paste. The bisque is dipped into the glaze paste, dried, and fired until the glaze materials melt and flow evenly over the surface.

3. The decoration. If the article is to be decorated, the design may be painted upon the body before glazing, or it may be painted upon the glaze and the article fired again, the pigments melting into the glaze. In the former case the pigments used are as a rule metallic oxides of various colors, while in the latter case they are often colored glasses.

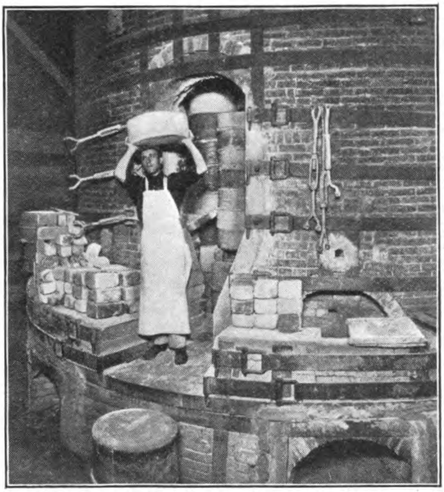


FIG. 163. The manufacture of pottery ; burning the ware in a kiln

Cement. The term *cement* as ordinarily used at present is applied to those mortars which possess the property of hardening in water as well as in air. These cements are silicate bodies, usually very highly basic in character, and when ground fine and mixed with water, they undergo complex reactions resulting in the formation of a hard, rocklike mass. A number of different classes of cements are known, the most important of which is called *Portland* cement.

Composition of Portland cement. The essential ingredients of Portland cement, together with the general limits of each ingredient, are as follows:

SiO_2	19 to 26%	MgO	0 to 5%
Al_2O_3	4 to 11%	SO_3	0 to 2.5%
Fe_2O_3	2 to 5%	Na_2O K_2O	0 to 3.0%
CaO	58 to 67%		

Manufacture of Portland cement. The materials most commonly employed are limestone or marl and clay or shale. In general, however, any substance may be used which furnishes the ingredients listed in the above table. Among the substances so used is blast-furnace slag, which is an impure calcium-aluminium silicate.

The materials to be used are coarsely ground and then mixed together in the proper proportions and finely pulverized. The resulting mixture is run into a furnace and burned to a temperature just short of fusion, at which temperature it vitrifies, forming a grayish mass known as *clinker*. Finally, the clinker is ground to a fine powder. Gypsum is often added in the process; this acts as a negative catalyzer, retarding the hardening, or setting, of the cement.

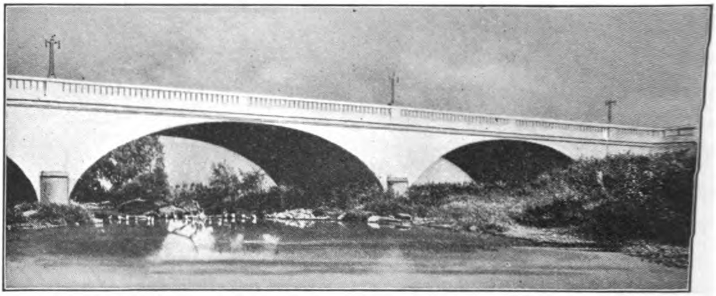


FIG. 164. A bridge built of reinforced concrete

The setting of cement. The reactions which take place upon the addition of water to cement, and which result in the formation of a hard, rocklike mass, are not thoroughly understood. The constituents of the cement apparently undergo hydrolysis when they come in contact with water. The resulting compounds unite with water producing hydrates. These hydrates are crystalline in character and form a hard, compact mass.

Growing importance of cement. Cement is rapidly coming into use for a great variety of purposes. It is often used in place of mortar in the construction of brick buildings. Mixed with crushed stone and sand it forms *concrete*, which is used in foundation work for buildings and street paving. It is also used in making artificial stone, terra cotta trimmings for buildings, artificial-stone walks and floors, fence posts, and the like. It is being used more and more for making articles which were formerly made of wood or stone, and the entire walls of buildings are sometimes made of cement blocks or of concrete. Iron rods or wire are often embedded in the concrete before it sets, to give it greater strength, and this is called *reinforced concrete.*

EXERCISES

1. In the manufacture of pottery why is the glaze made more fusible than the body of the ware?

2. Suppose that the glaze and the body expand and contract at different rates with changes in temperatures, what will be the result?

3. What is the meaning of the word *vitrify*?

4. What is a catalyzer? What is a *negative* catalyzer?

5. Why can cement be used as mortar in colder weather than ordinary mortar?

6. What is a polysilicic acid?

7. What weight of kaolin will result from the weathering of 1 ton of feldspar? *Ans.* 927 lb.

TOPICS FOR THEMES

The making of porcelain (Lassar-Cohn, Chemistry in Daily Life).

How cement is made (Rogers and Aubert, Industrial Chemistry).

The history of a china dish (Rogers and Aubert, Industrial Chemistry).

CHAPTER XXXVI

THE IRON FAMILY

Name	Symbol	Atomic Weight	Density	Melting Point	Oxides
Iron . . .	Fe	55.84	7.86	1530°	FeO, Fe_2O_3
Cobalt. . .	Co	58.97	8.6	1478°	CoO, Co_2O_3
Nickel. . .	Ni	58.68	8.9	1452°	NiO, Ni_2O_3

The family. The elements iron, cobalt, and nickel form a group in the eighth column of the periodic table. The atomic weights of the three are very close together, and their properties are very much alike.

IRON

Occurrence. The element iron has long been known, since its ores are very abundant and it is not difficult to prepare the metal from them in fairly pure condition. It occurs in large deposits as oxides, sulfides, and carbonates, and in smaller quantities in a great variety of minerals. Indeed, very few rocks or soils are free from small percentages of iron. It is a constituent of the chlorophyll of plants and the hæmoglobin of the blood of animals, and therefore plays an important part in life processes. Many meteorites are largely iron, usually alloyed with a little nickel.

Pure iron. Pure iron may be prepared by the electrolysis of a solution of iron sulfate between iron electrodes, though it is difficult to free it entirely from hydrogen in this way.

It is prepared in practically pure condition by the open-hearth method (p. 346). It is a silvery metal which melts at 1530°. It is ductile and malleable and almost as soft as aluminium. It is especially well adapted to the manufacture of electromagnets, since it acquires and loses magnetic properties more readily than do the ordinary varieties of iron. It is also used for purposes where resistance to corrosion is desired, for it does not rust rapidly.

The iron of commerce. Iron differs from most of the other metals used in the industries in that the pure metal is seldom obtained and is of limited application, while that containing small percentages of other elements exhibits a wide variety of properties which make it of the greatest value for many different purposes.

Carbon is always present in amounts which vary from a mere trace to about 7 per cent. According to the condition of treatment, the carbon may be in the form of graphite scattered through the iron, or it may occur as a solid solution of carbon in iron, or as carbides of iron, one of the most important of which has the formula Fe_3C, and is called *cementite.* Manganese, silicon, and traces of phosphorus and sulfur, together with a little oxygen, are also present.

The properties of the iron are so much modified by the percentages of these elements, by their form of combination, and by the treatment of the metal during its production, that many varieties of iron are recognized in commerce, the chief of which are *cast iron*, *wrought iron*, and *steel.*

Materials used in metallurgy of iron. Four different classes of materials are used in the metallurgy of iron:

1. ***Iron ore.*** The ores most frequently employed are the following:

Hematite	Fe_2O_3	Siderite . . .	$FeCO_3$
Magnetite	Fe_3O_4	Limonite . .	$2\,Fe_2O_3 \cdot 3\,H_2O$

While iron ore is mined in a number of different localities in the United States, the great center of production is in the neighborhood of Lake Superior, the ore being chiefly *hematite.* Large amounts are also mined near Birmingham, Alabama. Fig. 165 represents one of the large mines in Minnesota.

2. **Carbon.** Carbon in some form is necessary both as a *fuel* and as a *reducing agent.* In former times wood charcoal was used to supply the carbon, but now coke is almost universally used.

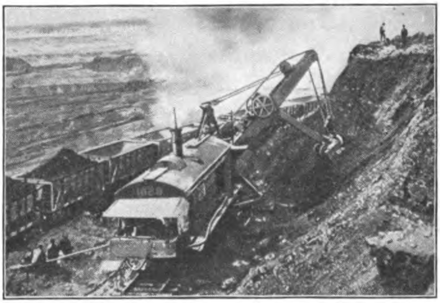


FIG. 165. Mining iron ore in Minnesota

3. **Hot air.** To maintain the high temperature required for the reduction of iron, a very active combustion of fuel is necessary. This is secured by forcing a strong blast of *hot air* into the lower part of the furnace during the reduction process.

4. **Flux.** All the materials which enter the furnace must leave it again, either in the form of gases or as liquids. The *iron* is drawn off as the liquid metal after its reduction, the *oxygen* with which it was combined escaping as oxides of carbon. To secure the removal of the *earthy matter* charged into the furnace along with the ore, materials are added to the charge which will combine with the impurities in the ore, forming a liquid. The material added for this purpose is called the *flux* and usually consists of limestone. The liquid produced from the flux and the ore is called *slag.* It is a variety of readily fusible glass.

Cast iron. Ordinarily the first step in the manufacture of any variety of commercial iron is the production of *cast iron.* The ores are mixed with a suitable flux, and are reduced by heating with coke.

Blast-furnace process. The reduction is carried out in a large tower, called a blast furnace (Fig. 166). This is usually 80 ft. high and 20 ft. in internal diameter at its widest part, narrowing somewhat toward both the top and the bottom. The walls are built of steel and are lined with fire brick. The base is provided with a number of pipes *A*, called *tuyères*, through which hot air is forced into the furnace. The tuyères are supplied from a large pipe *B*, which girdles the furnace. At the base of the furnace is an opening, through which the liquid metal can be drawn off from time to time. There is also a second opening *C*, somewhat above the first, through which the excess of slag overflows. The top is closed by a movable trap *D*, called the *cone*, and through this the materials to be used are introduced. The gases resulting from the combustion of the fuel and the reduction of the ore, together with the nitrogen of the air admitted through the tuyères, escape through pipes *E*. These gases are very hot and contain a sufficient percentage of carbon monoxide to render them combustible; they are accordingly utilized for heating the blast of air admitted through the tuyères, and as fuel for the engines.

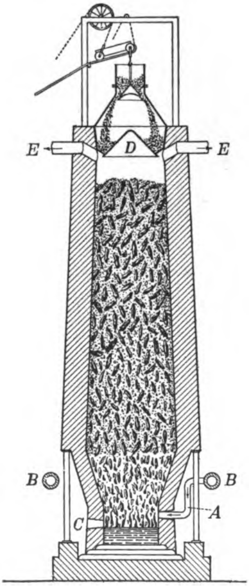


Fig. 166. Diagram of a blast furnace

Charges consisting of coke, ore, and flux in proper proportion are at intervals introduced into the furnace through the cone. The coke burns fiercely in the hot-air blast, forming carbon dioxide, which is at once reduced to carbon monoxide as it passes over the highly heated carbon.

Reduction of the ore begins at the top of the furnace through the action of the carbon monoxide. As the ore slowly descends, the reduction is completed, and the resulting iron melts and collects as a liquid in the bottom of the furnace, the lighter slag floating above it. After a considerable quantity of iron has collected, the slag is drawn off through *C*, and the iron is run into ladles and taken to the *converters* for the manufacture of steel; or it is run into sand molds and cast into ingots called *pigs*. Fig. 168 shows the method of drawing off the iron. A small hole is made near the bottom of the furnace, and the molten iron flows out and down the central channel *A* and into the sand molds along the sides *B*, where it solidifies.

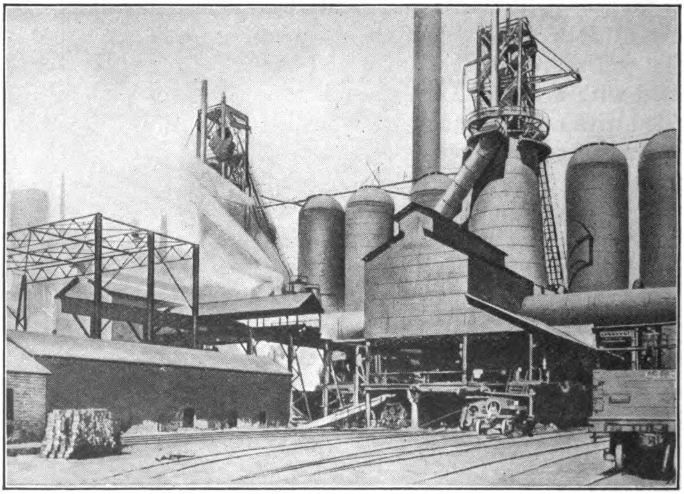


FIG. 167. A typical plant for the manufacture of cast iron

In practice, a number of furnaces are usually operated together, as illustrated in Fig. 167, which shows an exterior view of a modern plant for making cast iron.

Properties of cast iron. The iron produced in the blast furnace is called *cast iron.* It varies considerably in composition, but always contains over 2 per cent of carbon, variable amounts of silicon, and, at least, traces of phosphorus and sulfur. The form in which the carbon is present, whether free or combined, also greatly modifies the properties of the iron. In general, cast iron is hard and brittle, and melts at about 1100°. It cannot be welded or forged, but is easily cast in sand molds. It is rigid, but not elastic, and its tensile strength is small. It is used for making castings, but chiefly as a starting point in the manufacture of other varieties of iron.

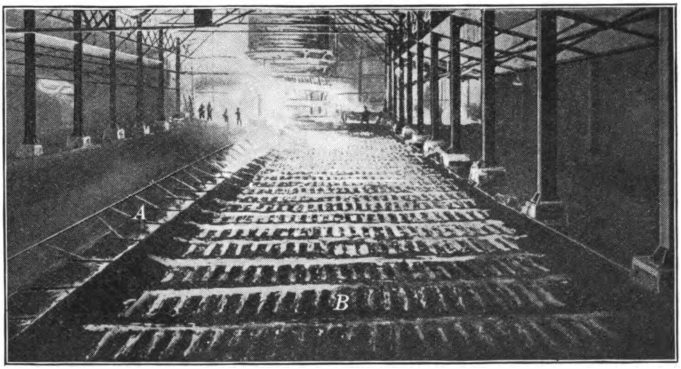


FIG. 168. Casting pig iron from a blast furnace

Wrought iron. Wrought iron is made from cast iron by burning out most of the carbon, silicon, phosphorus, and sulfur, the operation being conducted in what is called a *puddling furnace.*

Wrought iron is soft, malleable, and ductile. Its tensile strength is greater than that of cast iron, but less than that of most steel. Its melting point is much higher than that of cast iron, and if melted, it is changed into steel. It is no longer produced to the same relative extent as in former years, since soft steel can be made at a less cost and has almost the same properties.

Steel. Steel, like wrought iron, is made from cast iron by burning out a part of the carbon, silicon, phosphorus, and sulfur, but the processes used are quite different from that employed in the manufacture of wrought iron. Nearly all the steel of commerce produced in the United States is made by one of two general methods known as the *acid Bessemer process* and the *basic open-hearth process.*

Acid Bessemer process. In the acid Bessemer process the furnaces used are lined with *silica*, which, it will be recalled, is an *acid anhydride.* These furnaces remove from the cast iron the carbon and silicon, but not the phosphorus and sulfur. The process is therefore employed when the cast iron to be used is low in phosphorus and sulfur.

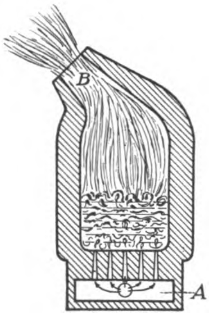


FIG. 169. Diagram of a Bessemer converter

Details of operation of Bessemer process. This process, invented about 1880, is carried out in great egg-shaped crucibles called *converters* (Fig. 169), each one of which will hold as much as 15 tons of steel. The converter is built of steel and lined with silica. It is mounted on trunnions, so that it can be tipped over on its side for filling and emptying. One of the trunnions is hollow, and a pipe connects it with an air chamber *A*, which forms a false bottom to the converter. The true bottom is perforated, so that air can be forced in by an air blast admitted through the trunnion and the air chamber.

White-hot liquid cast iron from a blast furnace is run into the converter through its open, necklike top *B*, the converter being tipped over to receive it; the air blast is then turned on, and the converter turned to a nearly vertical position. The carbon and silicon in the iron are rapidly oxidized (first the silicon and then the carbon), the oxidation being attended by a brilliant flame (Fig. 170). The heat of the reaction, largely due to the combustion of silicon, keeps the iron in a molten condition. The air blast is continued until the character of the flame shows that all the carbon has been burned away. The process requires from fifteen to twenty minutes, and when it is complete, the desired quantity of carbon (generally in the form of high carbon iron alloy) is added and allowed to mix thoroughly with the fluid. The converter is then tilted, and the steel run into molds, and the ingots so formed are hammered or rolled into rails or other objects.

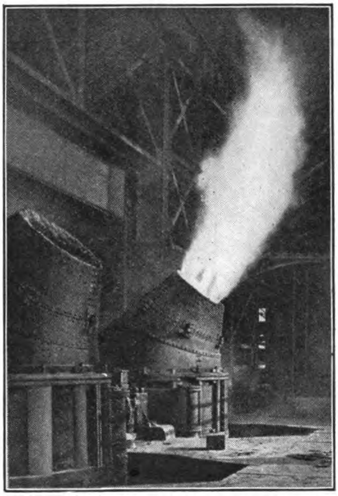


FIG. 170. A Bessemer converter in operation

Basic open-hearth process. In the basic open-hearth process the lining of the furnace is made of limestone or dolomite, both of which act as *bases*. In such furnaces the phosphorus and sulfur are both removed, as well as the silicon and carbon. The presence of more than traces of phosphorus and sulfur in the finished steel renders the metal so brittle that it is worthless. The open-hearth process, therefore, possesses a great advantage over the acid Bessemer process in that it makes it possible to utilize iron ores (or cast iron obtained from them) that contain appreciable quantities of phosphorus and sulfur. The operation does not need to be hastened, and steel of any desired composition can be produced.

Details of the open-hearth process. Fig. 171 shows the simpler parts of the type of furnace used in this process. The hearth of the furnace is about 40 ft. in length, 12 ft. in width, and 2 ft. in depth, and is lined with limestone or dolomite (*A*, *A*). Either gas or sprayed oil is used as fuel. Below the furnace is placed a checkerwork of brick so arranged that the hot products of combustion escaping from the furnace may be conducted through it, thus heating the bricks to a high temperature. Both the air necessary for combustion and the gaseous fuel (unless decomposed by heating, as in the case of natural gas and sprayed oil) are preheated by passing them over the hot bricks, so that the temperature reached during combustion is greatly increased.

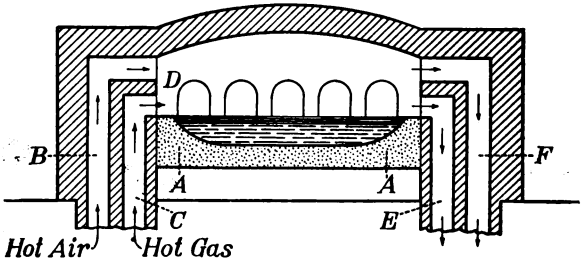


FIG. 171. Diagram of an open-hearth furnace

The gas entering through *C* comes in contact at *D* with the hot air entering through *B*, and a vigorous combustion results, the flame passing above and over the cast iron and lime with which the furnace is charged. The products of combustion escape through *E* and *F*. At the temperature reached, the carbon in the cast iron is removed in the form of the oxide, the escaping gas giving the melted metal the appearance of boiling. The silicon, phosphorus, and sulfur unite with oxygen to form acid anhydrides; these combine with the lime to form a slag, and this rises to the surface of the melted charge and is easily removed.

When a test shows that the desired percentage of carbon is present, the melted steel is run into large ladles and then into molds. An average furnace produces about 50 tons of steel in a given charge, approximately eight hours being required in the process. At present by far the largest amount of steel produced in the United States is made by this process.

Properties of steel. Steel contains from a trace up to 2 per cent of carbon, less than 0.1 per cent of silicon, and not more than traces of phosphorus and sulfur. When desired, a product containing as high as 99.85 per cent iron can be produced by the open-hearth method. Such steel is very soft, but resists rusting. As the percentage of carbon increases, the steel becomes harder and less ductile. Steel can be rolled into sheets, cast in molds, and forged into desired shapes.

The hardening and tempering of steel. When steel containing from 0.5 to 1.5 per cent of carbon is heated to a relatively high temperature and then cooled suddenly by plunging it into cold water or oil, it becomes very hard and brittle. When gradually reheated and then allowed to cool slowly, this hardened steel becomes softer and less brittle, and this process is known as *tempering.*

By properly regulating the temperature to which the steel is reheated in tempering, it is possible to obtain any condition of hardness demanded for a given purpose, as for making springs or cutting-tools. Steel assumes different color tints at different temperatures, and by these the experienced workman can tell when the desired temperature has been reached. Lake gives the following temperatures as suited to the tempering of the tools specified:

220°	paper cutters, wood-engraving tools
240°	knife blades, rock drills
260°	hand-plane cutters and cooper's tools
275°	axes, springs
290°	needles, screw drivers
300°	wood saws

Steel alloys. As we have seen (p. 339), small quantities of carbon greatly modify the properties of iron, and equally marked effects may be produced by a great many other elements. Accordingly, to secure a steel with the requisite properties, suitable percentages of these elements are added to the steel just before it is run out of the furnace. The elements most frequently added are manganese, silicon, nickel, chromium, tungsten, vanadium, and titanium, and steel containing an appreciable percentage of any of these elements is called a *steel alloy.* The element is added in the form of a rich alloy of iron, such as *ferrochromium* or *ferromanganese.*

The approximate composition and uses of some of the principal steel alloys is as follows:

3.5% nickel	armor plate
3.5% nickel and 3.5% chromium . . .	armor plate and projectiles
4.0% manganese	burglar-proof safes
6.0% chromium and from 8 to 24% tungsten	high-speed lathe tools
6.0% chromium and 10% molybdenum .	high-speed lathe tools
0.1% titanium	car rails and steel castings
0.1% vanadium	automobile parts

Steel purifiers. One great difficulty in securing a good steel is to prevent a slight oxidation at the end of the operation, together with the absorption of gases which cause blowholes as the casting solidifies. These difficulties are avoided, as far as possible, by adding to the steel, at the close of the operation, certain elements which will combine with the oxygen and the absorbed gases. The compounds formed pass into the slag, and almost none of the added element remains in the finished product. Aluminium is used to a large extent for this purpose as well as vanadium and titanium. Such elements are called *purifiers.*

Compounds of iron. Iron differs from the metals so far studied, in that it is able to form *two series* of compounds. In the one series the iron is *bivalent* and forms compounds which in formulas and many chemical properties are similar to the corresponding zinc compounds. These are called *ferrous* compounds. In the other series iron acts as a *trivalent* metal, and forms salts similar to those of aluminium. These salts are known as *ferric* compounds.

Ferrous salts. These salts are obtained by dissolving iron in the appropriate acid, or, when insoluble, by precipitation. The crystallized salts are usually light-green in color.

Ferrous sulfate ($FeSO_4$). Ferrous sulfate is the most familiar ferrous compound. It is usually obtained in the form of the hydrate $FeSO_4 \cdot 7\,H_2O$, called *copperas*, or *green vitriol*, and is prepared commercially as a by-product in the steel-plate mills. Preparatory to galvanizing or tinning (p. 370), steel plates are cleaned by immersing them in dilute sulfuric acid, and in the process some of the iron dissolves. The liquors are concentrated, and the green vitriol separates from them. The salt is used in the manufacture of ink and of iron alum, and as a reagent to destroy weeds.

Ferrous sulfide (FeS). Ferrous sulfide is sometimes found in nature as a golden-yellow crystalline mineral. It is formed as a black precipitate when a soluble sulfide and an iron salt are brought together in solution:

$$FeSO_4 + Na_2S \longrightarrow FeS + Na_2SO_4$$

It can also be made as a heavy dark-brown solid by fusing together the requisite quantities of sulfur and iron. It is used in the laboratory in the preparation of hydrogen sulfide (p. 145).

Iron disulfide (pyrite) (FeS_2). This substance occurs abundantly in nature in the form of brass-yellow cubical crystals and in compact masses. Sometimes it is called *fool's gold* from its superficial resemblance to the precious metal. It is used in very large quantities as a source of sulfur dioxide in the manufacture of sulfuric acid, since it burns readily in the air, forming ferric oxide and sulfur dioxide:

$$4\,FeS_2 + 11\,O_2 \longrightarrow 2\,Fe_2O_3 + 8\,SO_2$$

Ferrous carbonate ($FeCO_3$). This compound occurs in nature as *siderite* and is a valuable ore. Like calcium carbonate, it dissolves to some extent in water containing carbon dioxide, and waters containing it are called *chalybeate* waters.

Ferric salts. The crystallized ferric salts are usually yellow or violet in color. Heated with water in the absence of free acid, they hydrolyze even more readily than the salts of aluminium. The most familiar ferric salt is the chloride.

Ferric chloride ($FeCl_3$). This salt can be obtained most conveniently by dissolving iron in hydrochloric acid and then passing chlorine into the solution:

$$Fe + 2\,HCl \longrightarrow FeCl_2 + H_2$$
$$2\,FeCl_2 + Cl_2 \longrightarrow 2\,FeCl_3$$

The crystallized salt has the formula $FeCl_3 \cdot 6\,H_2O$.

Ferric hydroxide ($Fe(OH)_3$). When solutions of ferric salts are treated with ammonium hydroxide, ferric hydroxide is formed as a rusty-red precipitate insoluble in water.

Iron *rust* is a variable mixture of hydrated oxides of iron. When a film of rust forms on iron it does not protect the metal from the further action of water as does the rust of aluminium and zinc, because iron rust is porous and also tends to scale off, exposing a fresh surface.

Oxidation of ferrous salts. When a ferrous salt in the presence of an acid is oxidized to a ferric salt, it will be noticed that the valence of the iron is increased from 2 to 3. This increase in valence can often be brought about without the aid of oxygen, as is shown in the following equation:

$$2\,FeCl_2 + Cl_2 \longrightarrow 2\,FeCl_3$$

This is also called an oxidation, although no oxygen takes part in the reaction (p. 20), for the same product is obtained as by the other method:

$$2\,FeCl_2 + 2\,HCl + O \longrightarrow 2\,FeCl_3 + H_2O$$

In general, when the valence of the metallic ion of a salt is increased, the salt is said to be *oxidized*, whether any oxygen takes part in the reaction or not.

Reduction of ferric salts. Ferric salts may be changed into ferrous salts by the action of nascent hydrogen or other reducing agents, as shown in the following equations:

$$FeCl_3 + [H] \longrightarrow FeCl_2 + HCl$$
$$2\,FeCl_3 + Zn \longrightarrow 2\,FeCl_2 + ZnCl$$

Although no oxygen is removed (p. 31) in either of these reactions, the ferric chloride is said to be *reduced*; and, in general, when the valence of the metallic ion of a salt is diminished, the salt is said to be reduced.

Potassium ferrocyanide ($K_4FeC_6N_6$). When nitrogenous matter such as horns and refuse leather is heated with potassium carbonate and iron borings, and the mass is extracted with water, there crystallizes from the solution thus formed a beautiful lemon-yellow salt of the composition $K_4FeC_6N_6 \cdot 3\,H_2O$. This is called *potassium ferrocyanide* or *yellow prussiate of potash*. In solution it gives the ions $4\,K^+$ and $(FeC_6N_6)^{----}$ but no ions of iron. The ion

$(FeC_6N_6)^{----}$ acts as a radical, and many different ferrocyanides can be obtained by precipitation. For example, a ferric salt gives an intensely blue precipitate of ferric ferrocyanide:

$$3\,K_4(FeC_6N_6) + 4\,FeCl_3 \longrightarrow Fe_4(FeC_6N_6)_3 + 12\,KCl$$

This is called *Prussian blue.* It is used as a paint pigment and for bluing laundry water. Unless care is taken, the alkali of the soap will decompose the compound, forming ferric hydroxide and making rust stains.

Potassium ferricyanide ($K_3FeC_6N_6$). By treating a solution of potassium ferrocyanide with chlorine water and evaporating the solution to crystallization, garnet-red crystals are deposited which have the composition $K_3FeC_6N_6$:

$$2\,K_4FeC_6N_6 + Cl_2 \longrightarrow 2\,K_3FeC_6N_6 + 2\,KCl$$

This compound is called *potassium ferricyanide*, or *red prussiate of potash.*

Blue printing. When a ferric salt and potassium ferricyanide are brought together in solution, no precipitate forms, though the solution acquires a yellowish color. On exposure to the sunlight the ferric salt undergoes a partial reduction to ferrous salt, and a blue precipitate forms. Advantage is taken of these facts in the process of *blue printing.* A sensitive paper is prepared by soaking paper in a solution of potassium ferricyanide and a ferric salt (ferric ammonium citrate is generally used), and drying it in a dark place. When a black drawing on tracing cloth is placed upon such a sensitive paper and the two are exposed to the sunlight, the sensitive paper (except where it is protected by the black lines) turns a brownish color. It is then thoroughly washed with water, to remove the soluble salts, during which process the portions acted upon by the light turn blue, while the unaffected portions are left white. A solution of sodium hydroxide can be used as an ink for white lettering on a blue print, since this base decolorizes Prussian blue.

Other salts of iron. The following compounds of iron have industrial uses:

Ferric sulfate ($Fe_2(SO_4)_3$)	a white solid
Ferric nitrate ($Fe(NO_3)_3 \cdot 6\,H_2O$)	violet crystals
Iron alum ($NH_4Fe(SO_4)_2 \cdot 12\,H_2O$)	violet crystals

Inks. Most of the common black inks are made by treating an extract of *nutgalls* with ferrous sulfate and adding a blue-black dye. The nutgalls are rich in *tannic acid*, and this, with ferric compounds formed by the oxidation of the ferrous sulfate by the air, gives a nearly black precipitate. The black dye gives a temporary color, the permanent color being developed after the writing has been exposed to the air. The addition of some colloidal material, such as gum arabic or dextrin, together with a little sulfuric acid, delays the precipitation of the black substance in the bottle. A preservative is usually added, to prevent the ink from molding.

Removal of ink and other stains. Some stains may be removed by methods which involve no applications of chemistry. Thus, a grease spot may be removed by placing the stain over some blotting paper and washing it with carbon tetrachloride (p. 207) or benzine (p. 205). The grease is dissolved by the solvent, and the resulting solution is absorbed by the blotting paper. If the grease is a solid, such as candle grease or paraffin, it may be removed from the fabric by placing the stained portion between blotting papers and pressing it with a hot iron. The grease melts and is absorbed by the paper. Turpentine is a good solvent for paint spots, but must not be applied to silk. Many substances such as sirups may be washed out with water.

In many cases it is necessary to use chemical methods. Thus, the red color produced by many acids may be removed by washing the stained portion of the fabric with a little dilute ammonia water. Nitric acid acts upon the cloth as well as upon the dye, so that the original color cannot be restored. Coffee and fruit stains may usually be removed by placing the stain over a bowl and pouring boiling water upon it. If not removed in this way, the stain may be washed with a mild bleaching agent, such as bleaching powder, to which some water and a few drops of vinegar have been added. If the fabric is colored, the bleaching agent may act upon the dye, so that it is always wise in such cases first to try the effect of the agent upon a small clipping of the fabric.

Ink stains may be washed out with water, if treated at once, as in the case of fruit stains. When the ink has become dry and oxidized, the stain may be removed by treating with lemon juice or with a dilute solution of oxalic acid. By this treatment the ferric salts in the ink are reduced to ferrous salts which can then be washed out with water. Rust stains can be removed in a similar way. Some indelible-ink stains may be removed by soaking the fabric in a solution of sodium thiosulfate. *Silk is so sensitive to the action of solvents and reagents that it is generally impossible to remove stains from it without injuring the fabric.*

COBALT AND NICKEL

Occurrence. Cobalt and nickel are almost always found together in ores which also contain iron, silver, and copper, in combination with arsenic and sulfur. The richest deposits are in Ontario and New Caledonia. The extraction of these metals from their ores and their separation from each other is too complicated a process to be described here. Nickel is also a frequent impurity of crude copper, and several million pounds of nickel sulfate are annually recovered in the United States in the refining of copper by electrolysis.

Properties and uses. Both these metals are silvery in appearance and take a high polish. They are somewhat heavier than iron, and melt at a lower temperature. Their chief use is in making alloys. An alloy of cobalt and chromium is used for making cutlery and lathe tools. Nickel coinage consists of 75 per cent copper and 25 per cent nickel. German silver (p. 360) also contains about 25 per cent nickel. Nickel is extensively used as a plating upon other metals (particularly upon brass), to prevent tarnishing in air, and cobalt can be used in the same way.

Electroplating with nickel. Nickel plating is accomplished by an electrolytic process. The electrolyte consists of a solution of nickel ammonium sulfate, a salt having the composition $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$. The object to be plated is suspended in the electrolyte and serves as the cathode, while a plate of nickel is used as the anode. When the current is passing through the electrolyte, the nickel is deposited upon the object to be plated, and an equivalent portion of nickel dissolves from the anode, the composition of the electrolyte remaining unchanged. Fig. 172 illustrates the process carried out on a large scale, the objects to be plated being suspended from the rods *A*, *A*.

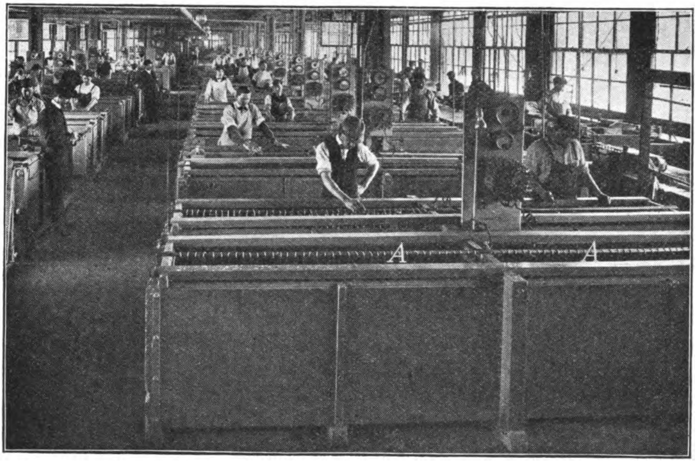


FIG. 172. Electroplating with nickel

Cobalt oxide (CoO). This is the form in which most of the cobalt comes into the market. It is a black powder used in making other cobalt compounds, and in making blue glass and blue decorations on china. Sometimes ground blue cobalt glass, called *smalt*, is used instead of the oxide, and as a pigment.

Salts of cobalt and nickel. Nearly all the simple salts of cobalt and of nickel have formulas similar to those of *ferrous* salts. The most familiar are the following:

$Co(NO_3)_2 \cdot 6\,H_2O$	a cherry-red deliquescent salt
$CoCl_2 \cdot 6\,H_2O$	similar in appearance to the nitrate
CoS	an insoluble black precipitate
$NiSO_4 \cdot 7\,H_2O$	well-formed green crystals
$Ni(NO_3)_2 \cdot 6\,H_2O$	deliquescent green crystals
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$	used in nickel plating
NiS	an insoluble black precipitate

EXERCISES

1. Why does not iron occur in native state? What does its native occurrence in meteors indicate?

2. Why is the furnace in which cast iron is made called a blast furnace?

3. If cast iron contained no carbon or silicon, could it be worked in a Bessemer converter?

4. Why is the air heated before it is admitted to a blast furnace?

5. Write equations for the oxidation of ferrous nitrate to ferric nitrate in the presence of nitric acid.

6. Write equations for the reduction of ferric sulfate by nascent hydrogen.

7. Calculate the weight of iron which can be produced from 1 ton of hematite. *Ans.* 1398.8 lb.

8. What is the meaning of the term *magnetite*?

9. What are some of the advantages of plating brass with nickel?

10. Calculate the percentage of iron in hematite, in magnetite, and in siderite. *Ans.* 69.94; 71.92; 48.20.

TOPICS FOR THEMES

The making of a nail (see encyclopedia).
The making of a needle (see encyclopedia).
How iron castings are made. (Visit a foundry.)

CHAPTER XXXVII

COPPER, MERCURY, AND SILVER

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	FORMULAS OF OXIDES	
					ous	*ic*
Copper . .	Cu	63.57	8.93	1083°	Cu_2O	CuO
Mercury .	Hg	200.60	13.56	– 38.7°	Hg_2O	HgO
Silver . .	Ag	107.88	10.50	960.5°	Ag_2O	AgO

The family. Although mercury is not in the same family with copper and silver, the three elements resemble each other so closely in chemical conduct that it is convenient to class them together for study.

COPPER

Occurrence. The element copper has been used for various purposes since the earliest days of history. It is often found in the native state, large masses of it occurring nearly pure in the Lake Superior region and, to a smaller extent, in other places. The most valuable ores are the following:

SULFUR ORES		OXYGEN ORES	
Chalcopyrite . . .	$CuFeS_2$	Cuprite . .	Cu_2O
Chalcocite	Cu_2S	Melaconite .	CuO
Bornite	Cu_3FeS_3	Malachite .	$CuCO_3 \cdot Cu(OH)_2$

Metallurgy of copper. Ores containing little or no sulfur are easy to reduce. They are first crushed and the earthy impurities washed away. The concentrated ore is then mixed with carbon and heated in a furnace, metallic copper resulting from the reduction of the copper oxide by the hot carbon.

Metallurgy of sulfur ores. Much of the copper of commerce is made from chalcopyrite and bornite, and these ores are more difficult to work. They are first *roasted* in the air, by which treatment some of the iron is converted into oxide. Care is taken, however, to leave enough sulfur to combine with *all* of the copper and with a *part* of the iron.

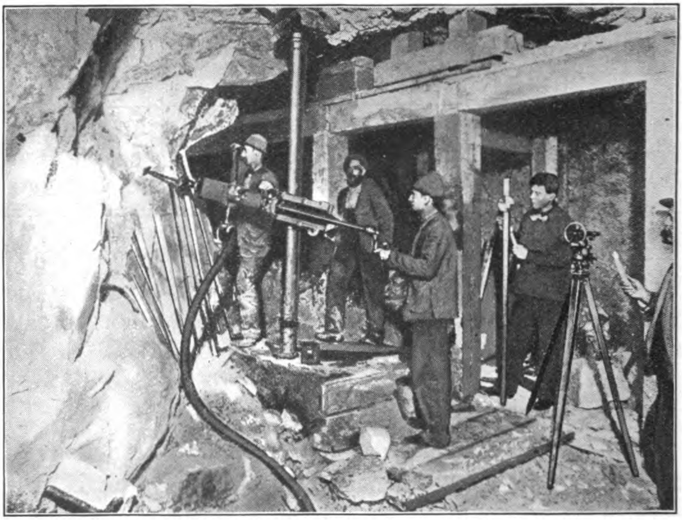


Fig. 173. Mining copper ore at Butte, Montana

The ore so treated (or coarse ore which needs no treatment), together with a flux rich in silica, is charged into a furnace called a *matte* furnace. In this, the iron oxide combines with the silica to form a liquid slag, while the sulfides of iron and copper melt into a heavier liquid called *matte.*

The liquid matte is then tapped off into a *converter* closely resembling the one used in the Bessemer process and holding from 6 to 10 tons. Some silica is added, and a carefully regulated current of air is blown in. The sulfur acts as fuel, burning to form sulfur dioxide; the iron sulfide is converted into oxide, which then combines with the silica to form slag; the copper sulfide burns to form sulfur dioxide and copper. When the process is complete, the copper is poured into molds. It is called *blister* copper, and may be as high as 98 per cent pure. The United States at present produces about 1,500,000,000 lb. of copper annually.

Refining of copper. Blister copper is purified by electrolysis. A large plate of it, serving as an anode, is suspended in a tank, facing a thin plate of pure copper which is the cathode. The tank is filled with a solution of copper sulfate and sulfuric acid to act as the electrolyte. A current from a dynamo passes from the anode to the cathode, and the copper, dissolving from the anode, is deposited upon the cathode in pure form, while the impurities collect on the bottom of the tank. Electrolytic copper is one of the purest of commercial metals.

Recovery of gold and silver. Gold, silver, and nickel are often present in small quantities in copper ores, and remain in the crude copper. In electrolytic refining the gold and silver collect in the muddy deposit on the bottom of the tank. The mud is carefully worked over from time to time and the precious metals extracted from it. A surprising amount of gold and silver is obtained in this way. The nickel passes into solution and is recovered from the electrolyte.

Properties of copper. Copper is a rather heavy metal of density 8.9, and has a characteristic reddish color. It is rather soft, and is very malleable, ductile, and flexible, yet tough and strong; it melts at 1083° and boils at 2310°. As a conductor of heat and electrical energy it is second only to silver.

Since it is below hydrogen in the displacement series, hydrochloric acid, dilute sulfuric acid, and fused alkalies are almost without action upon it; nitric acid and hot concentrated sulfuric acid, however, readily dissolve it (pp. 130, 148). In moist air it slowly becomes covered with a film of the bright-red oxide Cu_2O, which soon changes to a green basic carbonate. Heated in the air the metal is easily oxidized to the black oxide CuO.

Uses. Copper is extensively used for electrical purposes, for roofs and cornices, for sheathing the bottoms of ships, and for making alloys. In the following table the composition of some of these alloys is indicated:

Aluminium bronze . .	90%–98% copper, 2%–10% aluminium
Brass	63%–73% copper, 27%–37% zinc
Bronze	70%–95% copper, 1%–25% zinc, 1%–18% tin
German silver . . .	50%–60% copper, 20% zinc, 20%–30% nickel
Gun metal	90% copper, 10% tin
Gold coin	10% copper, 90% gold
Silver coin	10% copper, 90% silver
Nickel coin	75% copper, 25% nickel

Electrotyping. Books are often printed from electrotype plates, which are prepared as follows: The face of the type is covered with wax, and this is firmly pressed down until a clear impression is obtained. The impressed side of the wax is coated with graphite, and this is made the cathode in an electrolytic cell containing a copper salt in solution. The copper is deposited as a thin sheet upon the letters in wax and, when detached, is a perfect copy of the type, the under part of the letters being hollow. The sheet is strengthened by pouring on the undersurface a suitable amount of commercial lead. The sheet so strengthened is then used in printing.

Two series of copper compounds. Copper, like iron, forms *two series* of compounds: the *cuprous* compounds, in which it is univalent; and the *cupric* compounds, in which it is bivalent. The cupric salts are much the more common of the two.

Cuprous compounds. The most important cuprous compound is the oxide Cu_2O, which occurs in nature as *ruby copper*, or *cuprite*. It is a bright-red substance and can easily be prepared by heating copper to a high temperature in a limited supply of air. It is used for imparting a ruby color to glass. By treating cuprous oxide with different acids a number of cuprous salts can be made.

Cupric compounds. Cupric salts are easily made by dissolving cupric oxide in acids, or, when insoluble, by precipitation. In crystallized form most of them are blue or green. Since they are so much more familiar than the cuprous salts, they are frequently called merely copper salts.

Cupric oxide (CuO). This is a black insoluble substance obtained by heating copper in excess of air, or by igniting the hydroxide or the nitrate. It is used as an oxidizing agent.

Cupric sulfate ($CuSO_4$). When crystallized from water, copper sulfate forms large blue crystals of the hydrate $CuSO_4 \cdot 5\,H_2O$, called *blue vitriol*, or *bluestone*. The salt is a by-product in silver refining, and is also made by the oxidation of pyrite containing copper:

$$CuS + 2\,O_2 \longrightarrow CuSO_4$$

The salt finds extensive use in electrotyping, in copper refining, as a remedy for hoof diseases (particularly in sheep), and in the manufacture of insecticides (p. 255). Like all copper salts, it is poisonous, especially to lower forms of life. When added, even in very minute quantities, to water containing green pond scum (algæ), the plant is quickly killed. Mixed with milk of lime (which precipitates copper hydroxide), it is called *Bordeaux mixture*, and is used as a spray for killing molds and scale on fruit trees.

Cupric sulfide (CuS). In the form of a black insoluble precipitate cupric sulfide (CuS) is easily prepared by the action of hydrogen sulfide upon a solution of a copper salt:

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4$$

MERCURY

Occurrence. Mercury occurs in nature chiefly as the sulfide HgS, called *cinnabar*. The mercury mines of Spain have long been famous, and California is the next largest producer.

Metallurgy. Mercury is a volatile metal which has but little affinity for oxygen, and this makes the metallurgy of mercury very simple. The crushed ore, mixed with a small amount of carbon to reduce any oxide or sulfate that might be formed, is roasted in a current of air. The sulfur burns to sulfur dioxide, while the mercury vaporizes and is condensed in a series of condensing vessels. The metal is purified by distillation.

Properties. Mercury is a heavy, silvery liquid, with a density of 13.56. It boils at 357° and solidifies at $-38.7°$. It forms alloys (called amalgams) with nearly all metals.

Toward acids mercury conducts itself very much like copper; it is easily attacked by nitric acid and by hot concentrated sulfuric acid, while cold sulfuric acid and hydrochloric acid have no effect on it.

Uses. Mercury is extensively used in the construction of many scientific instruments, such as the thermometer and the barometer, and as a liquid over which to collect gases that are soluble in water. The readiness with which it alloys with silver and gold makes it very useful in the extraction of these elements. All salts of mercury are made directly or indirectly from the purified metal.

Compounds of mercury. Like copper, mercury forms two series of compounds: the *mercurous* compounds, of which mercurous chloride ($HgCl$) is an example; and the *mercuric* compounds, represented by mercuric chloride ($HgCl_2$).

Mercuric oxide (HgO). Mercuric oxide is usually obtained as a brick-red substance by carefully heating the nitrate:

$$2\,Hg\,(NO_3)_2 \longrightarrow 2\,HgO + 4\,NO_2 + O_2$$

It can also be obtained in a yellow form. When heated, the oxide darkens until it becomes almost black; at a higher temperature it decomposes into mercury and oxygen (p. 4).

Mercurous chloride (calomel) ($HgCl$). Being insoluble, mercurous chloride is precipitated as a white solid when a soluble chloride is added to a solution of mercurous nitrate:

$$HgNO_3 + NaCl \longrightarrow HgCl + NaNO_3$$

Commercially, it is manufactured by heating a mixture of mercuric chloride and mercury. It is a common medicine.

Mercuric chloride (corrosive sublimate) ($HgCl_2$). This substance can be made by dissolving mercuric oxide in hydrochloric acid. On a commercial scale it is made by heating a mixture of common salt and mercuric sulfate:

$$2\,NaCl + HgSO_4 \longrightarrow HgCl_2 + Na_2SO_4$$

The mercuric chloride, being readily volatile, vaporizes, and is condensed again in cool vessels. It is like mercurous chloride in being a white solid, but is soluble in water. It is extremely poisonous, and in dilute solutions is used as an antiseptic in dressing wounds.

Mercuric sulfide (HgS). As cinnabar, this substance forms the chief native compound of mercury, and occurs in red crystalline masses. By passing hydrogen sulfide into a solution of a mercuric salt, mercuric sulfide is precipitated as a *black* powder insoluble in water and acids. By other means it can be prepared as a brilliant red powder, known as *vermilion*, which is used as a pigment in fine paints.

SILVER

Occurrence. Silver is found in small quantities in the uncombined state; usually, however, it occurs in combination with sulfur, either as the sulfide Ag_2S or as a constituent of other sulfides, especially those of lead and copper. It is also found alloyed with gold.

In this country silver is produced almost entirely in connection with lead, and it will be convenient to consider the metallurgy of the two metals together in the next chapter.

The refining of silver. Crude silver obtained by any process may contain a number of metals, especially copper and gold, and is usually refined by *parting* with sulfuric acid. The alloy is heated with concentrated sulfuric acid, which dissolves the silver and copper, but not the gold. In the solution of silver sulfate so obtained, copper plates are suspended upon which pure silver precipitates, the copper going into solution as the sulfate, as shown in the equation

$$Ag_2SO_4 + Cu \longrightarrow 2\,Ag + CuSO_4$$

The solution obtained as a by-product in this process furnishes much of the blue vitriol of commerce. Silver is also refined by electrolytic methods similar to those used in the refining of copper.

Properties of silver. Silver is a heavy, rather soft, white metal, very ductile and malleable, and capable of taking a high polish. It surpasses all other metals as a conductor of heat and electricity, but is too costly to find extensive use for such purposes. It melts at a little lower temperature than copper. It alloys readily with other heavy metals, and when it is to be used for coinage or for tableware, a small amount of copper — from 8 per cent to 10 per cent — is melted with it to give it hardness (sterling silver).

It is not acted upon by water or air, but is quickly tarnished when in contact with sulfur compounds (eggs, mustard, perspiration), turning quite black in time. Hydrochloric acid and fused alkalies do not act upon it, but nitric acid and hot concentrated sulfuric acid dissolve it with ease. When a solution of a silver salt is treated with a strong reducing agent, metallic silver is precipitated. Under proper conditions this takes the form of a brilliant mirror deposited on the sides of the glass vessel. *Mirrors* are usually made in this way.

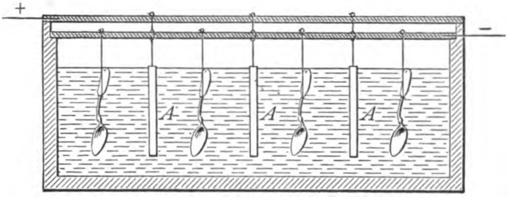


FIG. 174. The process of silver plating

Electroplating with silver. Since silver is not acted upon by water or air, and has a pleasing appearance, it is used to coat various articles made of cheaper metals. Such articles are said to be *silver plated*, and the process by which this is done is very similar to electroplating with nickel (p. 355). The object to be plated (as, for example, a spoon) is attached to a wire and dipped into a solution of a suitable silver salt. Electrical connection is made in such a way that the article to be plated is the cathode (Fig. 174), while the anode *A* is made up of one or more plates of silver.

Compounds of silver. Silver forms only one series of salts, which corresponds to the mercurous and the cuprous series.

Silver nitrate (lunar caustic) ($AgNO_3$). This salt is easily prepared by dissolving silver in nitric acid, and evaporating the resulting solution. It crystallizes in flat colorless plates, and when heated carefully can be melted without decomposition. When cast into sticks it is called *lunar caustic*, for it has a very corrosive action on flesh, and is sometimes used in surgery to burn away abnormal growths.

The alchemists designated the metals by the names of the heavenly bodies. The moon (*luna*) was the symbol for silver; hence the name *lunar caustic*.

Silver sulfide (Ag_2S). This occurs in nature and constitutes one of the principal ores of silver. It can be obtained as a black solid by heating silver and sulfur together or by passing hydrogen sulfide into a solution of silver nitrate.

Compounds of silver with the halogens. The chloride, bromide, and the iodide of silver are insoluble in water and in acids, and therefore are precipitated by bringing together a soluble halogen salt with silver nitrate:

$$AgNO_3 + KCl \longrightarrow AgCl + KNO_3$$

They are remarkable for the fact that they are very sensitive to the action of light, undergoing a change of color and chemical composition when exposed to sunlight, especially if in contact with organic matter, such as gelatin. It is upon this property of the silver halides that the art of photography is based.

Photography. From a chemical standpoint the processes of photography may be described under two heads: (1) the preparation of the negative; (2) the preparation of the print.

1. ***Preparation of the negative.*** The plate used in the preparation of the negative is made by spreading a thin layer of gelatin, in which colloidal silver bromide is suspended (silver iodide is sometimes added also), over a glass plate or celluloid

film and allowing it to dry. When the plate so prepared is placed in a camera and the image of some object is focused upon it, the silver salt undergoes a change which is proportional at each point to the intensity of the light falling upon it. In this way an image of the object photographed is produced upon the plate. This image, however, is invisible and is therefore called latent. It can be made visible by the process of *developing*.

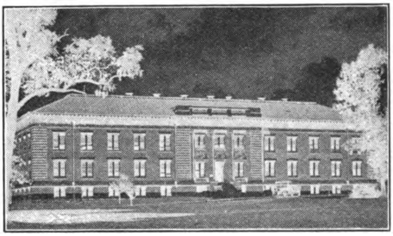


FIG. 175. The negative plate

To develop the image the exposed plate is immersed in a solution of some reducing agent called the *developer*. While the developer will *in time* reduce all the silver salt, it acts much more rapidly upon that which has been exposed to the light. The action is therefore continued only long enough to bring out the image. The reduced silver is deposited in the form of a black film which adheres closely to the plate.

The unaffected silver salt is now removed from the plate by immersing it in a solution of sodium thiosulfate (*hypo*). The plate is then washed with water and dried. The plate so prepared is called the *negative* (Fig. 175), because it is a picture of the object photographed, with the lights and positions exactly reversed.

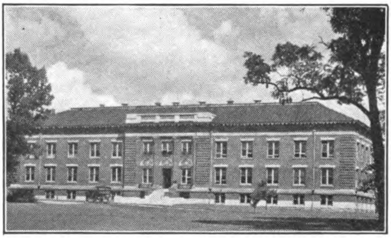


FIG. 176. The positive print

2. **Preparation of the print.** The print is made on paper which is prepared much in the same way as the negative plate. The negative is placed upon this paper and exposed to the light in such a way that the light must pass through the negative before striking the paper. If the paper is coated with silver chloride,

a visible image is produced, in which case a developer is not needed. *Proofs* are made in this way. In order to make them permanent, the unchanged silver chloride must be dissolved off with sodium thiosulfate. The print is then *toned* by dipping it into a solution of gold or platinum salts, in which process the silver on the print passes into solution, while the gold or platinum takes its place. These metals give a characteristic color or tone to the print, the gold making it reddish brown, while the platinum gives it a steel-gray tone. Since the darkest places on the negative cut off the most light, it is evident that the lights of the print (Fig. 176) will be the reverse of those of the negative, and will therefore correspond to those of the object photographed.

EXERCISES

1. Why has copper or bronze been used for so long a time?

2. Why do we have so many relics from the bronze age and so few from the iron age?

3. Why is a solution of copper sulfate acid to litmus paper?

4. How would you account for the fact that so many different salts of copper have the same blue color in dilute solutions?

5. How could you distinguish between mercurous chloride and mercuric chloride?

6. Crude silver usually contains iron and lead. What would become of these in refining silver by *parting* with sulfuric acid?

7. Mercuric nitrate and silver nitrate are both white soluble solids. How could you distinguish between them?

8. How do you account for the fact that a silver spoon gradually darkens when in contact with eggs?

9. Why are all three of these metals found to some extent native in nature?

10. What properties make mercury useful in thermometers and in barometers?

Topics for Themes

The history of a Kodak picture (Lassar-Cohn, Chemistry in Daily Life).

How mirrors are made (Lassar-Cohn, Chemistry in Daily Life).

How thermometers are made (see encyclopedia).

CHAPTER XXXVIII

TIN AND LEAD

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	COMMON OXIDES
Tin . .	Sn	119.0	7.3	232°	SnO SnO_2
Lead .	Pb	207.1	11.37	327°	PbO Pb_3O_4 PbO_2

TIN

Occurrence. Tin is found in nature chiefly as the oxide SnO_2, called *cassiterite*, or *tinstone*. The most famous mines are in Cornwall, in the East Indies, and in Bolivia. Very little is produced in the United States.

Metallurgy. The metallurgy of tin is very simple. The ore, separated as far as possible from earthy materials, is mixed with carbon and heated in a furnace, the reduction taking place readily. The equation is

$$SnO_2 + C \longrightarrow Sn + CO_2$$

The metal is often purified by carefully heating it until it is partly melted; the pure tin melts first and can be drained away from the impurities.

Properties. Pure tin, called *block* tin, is a soft white metal with a silver-like appearance and luster; it melts readily (232°) and is somewhat lighter than copper, having a density of 7.3. It is malleable and can be rolled out into very thin sheets, forming *tin foil*; most tin foil, however, contains a marked percentage of lead.

Under ordinary conditions tin is unchanged by air or moisture, but at a high temperature it burns, forming the oxide SnO_2. Dilute acids have little effect upon it, but concentrated acids attack it readily. Concentrated hydrochloric acid changes it into the chloride:

$$Sn + 2\,HCl \longrightarrow SnCl_2 + H_2$$

With sulfuric acid, tin sulfate and sulfur dioxide are formed:

$$Sn + 2\,H_2SO_4 \longrightarrow SnSO_4 + SO_2 + 2\,H_2O$$

Concentrated nitric acid oxidizes it, forming a white insoluble compound, H_2SnO_3, called *metastannic acid.*

Uses of tin. A great deal of tin is used in the making of *tin plate.* The process consists in dipping thin sheets of iron into the melted tin and is quite similar to that of galvanizing iron (p. 319). Owing to its resistance to the action of air and weak acids, tin plate is used in many ways, such as in roofing, and in the manufacture of tin cans, cooking vessels, and similar articles. Small pipes of block tin are used instead of lead for conveying pure water or liquids containing dilute acids, such as soda water. Many useful alloys contain tin (p. 360). *Pewter* and *soft solder* are alloys of tin and lead.

Soldering and brazing. The use of solder in joining two metal surfaces depends upon (1) the low melting point of the solder, and (2) the fact that it flows over *clean* metal surfaces and sticks to them on cooling. To secure clean surfaces free from oxide, a suitable flux must be used which will either *dissolve* the oxide as fast as it forms, or will *reduce* it again to metal. The usual fluxes are zinc chloride, ammonium chloride, rosin, and stearin. In *brazing* or *hard soldering* the process is essentially the same, except that a low-melting brass is used instead of solder, and borax is used as a flux.

Compounds of tin. Tin forms two series of metallic compounds: the *stannous*, in which the tin is bivalent, as is illustrated in the compounds SnO, SnS, $SnCl_2$; and the *stannic*, in which it is tetravalent, as shown in the compounds SnO_2, SnS_2.

Chlorides of tin. *Stannous* chloride is prepared by dissolving tin in concentrated hydrochloric acid and evaporating the solution to crystallization. The crystals which are obtained have the composition $SnCl_2 \cdot 2\,H_2O$, and are known as *tin crystals*. By treating a solution of stannous chloride with aqua regia, *stannic* chloride is formed:

$$SnCl_2 + 2\,Cl \longrightarrow SnCl_4$$

The salt which crystallizes from such a solution has the composition $SnCl_4 \cdot 5\,H_2O$, and is known commercially as *oxymuriate of tin*. If metallic tin is heated in a current of dry chlorine, *anhydrous* stannic chloride ($SnCl_4$) is obtained as a heavy, colorless liquid which fumes strongly on exposure to air. A great deal of tin in the form of stannic chloride is recovered from scrap tin by the action of chlorine.

The crystallized chlorides of tin are much used as mordants in dyeing processes, and in calico printing.

LEAD

Occurrence. Lead is found in nature chiefly as the sulfide PbS, called *galenite* (Fig. 178). In the United States this is mined principally in Missouri (Fig. 177) and Idaho.

Metallurgy of lead. Almost all the lead of commerce is made from galenite, which usually contains some silver. To obtain this silver most economically it is customary to combine richer silver ores with lead ores and work the two together.

Reduction of silver-bearing lead. The sulfide ores are first roasted until a part of the sulfide has been changed into the oxide and the sulfate. The air is then shut off and the heating continued, which brings about the reactions indicated in the following equations:

$$2\,PbO + PbS \longrightarrow 3\,Pb + SO_2$$
$$PbSO_4 + PbS \longrightarrow 2\,Pb + 2\,SO_2$$

By reactions which are similar to the above, the ores bearing silver are reduced, the silver alloying with the lead.

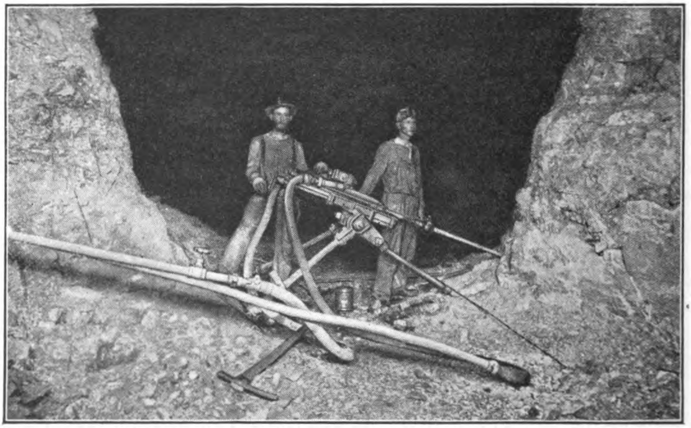


FIG. 177. Mining galenite in the Joplin region in Missouri

The softening of lead. The lead obtained in this way is called *hard* lead, and in addition to silver contains smaller quantities of other elements, especially of copper, arsenic, antimony, gold, and bismuth. The lead is *softened* by melting it in an open furnace with free access of air. This converts most of the impurities (as well as some lead) into oxides which float upon the melted lead and can easily be removed. The partially purified lead is called *soft* lead.

Desilverizing of lead (the Parkes process). The lead is melted in large kettles holding as much as 30 tons, and about 1 per cent of zinc is stirred in. These two metals do not mix to any great extent, and gold, silver, and copper are much more soluble in zinc than in lead. Consequently when the stirring ceases, the zinc rises to the surface of the lead, carrying with it the other metals. The zinc is then skimmed off and distilled (by which process the zinc is recovered to be used again), and the residue of silver and gold is melted down and cast into ingots called *doré* bars. These are refined as explained under silver (p. 364). An electrolytic method (*Betts process*) is now being used, similar to the one employed with copper, but with many special details.

Properties. Lead is a heavy metal which has a brilliant silvery luster on a freshly cut surface, but which soon tarnishes by oxidation to a dull blue-gray color. It is soft, easily fused (melting at 327°), and malleable, but has little toughness or strength.

It is not acted upon to any great extent, under ordinary conditions, by the oxygen of the air, but at a high temperature is changed into the oxide. With the exception of hydrochloric and sulfuric acids (which form insoluble compounds), most acids, even very weak ones, act upon it, forming soluble lead salts. Hot concentrated hydrochloric and sulfuric acids also attack it to a slight extent.

Uses. Lead finds many important applications in the industries, chiefly in the manufacture of storage batteries, in linings for sulfuric acid plants, in alloys of various kinds (such as shot, antifriction metals, type metal, and pewter), and in water pipes for plumbing. Since lead dissolves to some extent in pure water, it should not be used for pipes that are to carry rain water. About one third of the annual production of lead is used in making paint, and is permanently lost.

Compounds of lead. In nearly all its compounds lead is bivalent, but in a few of its compounds it has a valence of four. All of its compounds are poisonous.

Lead oxides. Lead forms a number of oxides, the most important of which are the following:

1. ***Litharge (PbO).*** This oxide forms when lead is oxidized at a rather low temperature, and is obtained as a by-product in silver refining. It apparently exists in a number of different forms ranging from yellow and light brown to red. It has a number of commercial uses.

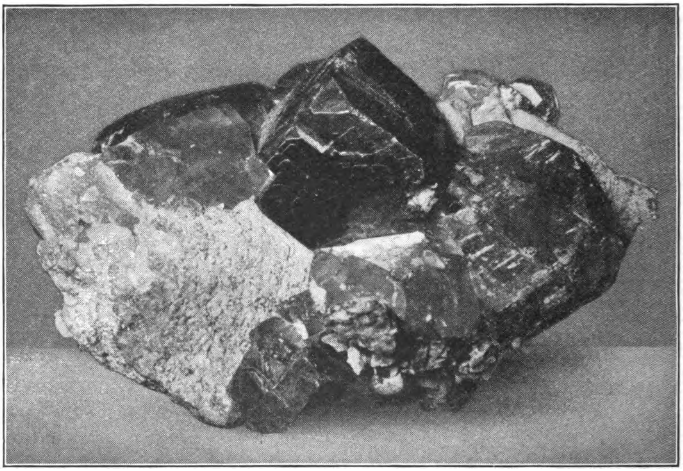


FIG. 178. A crystal of galenite embedded in calcite

2. ***Red lead, or minium*** **(Pb_3O_4).** Minium is prepared by heating lead (or litharge) to a high temperature in contact with a current of air. It is a heavy powder of a beautiful red color and is much used as a pigment for painting structural iron. Mixed with linseed oil it forms a cement used in joining gas pipes.

3. ***Lead peroxide (PbO_2).*** This is left as a residue when minium is heated with nitric acid. It is a brown powder which easily gives up a part of its oxygen and is a good oxidizing agent.

Lead sulfide (PbS). In nature this compound occurs in a highly crystalline form called *galenite* (Fig. 178), the crystals having much the same color and luster as pure lead. It is readily prepared in the laboratory as a black precipitate, by the action of hydrogen sulfide upon soluble lead salts:

$$Pb(NO_3)_2 + H_2S \longrightarrow PbS + 2\,HNO_3$$

It is insoluble both in water and in dilute acids.

Lead carbonate. While the normal carbonate of lead, $PbCO_3$, is found to some extent in nature and can be prepared in the laboratory, basic carbonates of varying composition are much more easy to obtain. One of the simplest of these has the composition $(PbCO_3)_2 \cdot Pb(OH)_2$, and is called *white lead.* This is prepared on a large scale as a white pigment and as a body for paints which are to be colored with other substances.

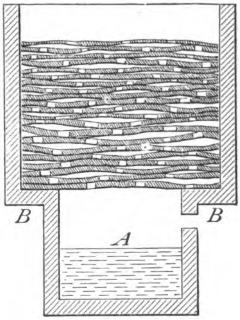


FIG. 179. A crock containing lead plates for making white lead

Manufacture of white lead. White lead can be prepared by a number of processes, but no other seems to produce a product of as desirable physical properties as the old Dutch process, which has been used for centuries, though with many improvements. In this process the lead is cast into perforated plates called *buckles*, which are placed loosely upon each other in a crock of the shape shown in Fig. 179, the ledge *B* formed by the constriction of the crock supporting the plates. Under them in *A* is poured a suitable quantity of dilute acetic acid, and the crocks so charged are placed in banks and covered with stable manure or spent tanbark. The heat of fermentation in the latter warms the acid, the fumes of which attack the lead, forming lead acetate. The carbon dioxide from the fermentation enters into reaction with the acetate and produces the basic carbonate, regenerating acetic acid, which acts again upon the lead. The process continues until the buckles are almost completely converted into the desired compound. Fig. 180 shows a buckle before and after the corrosion.

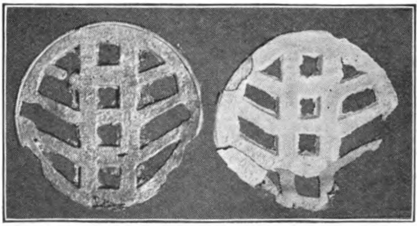


FIG. 180. Lead buckle before and after exposure to acetic acid and carbon dioxide

Paints. A paint consists of three essential ingredients: the vehicle, the body, and the pigment.

1. ***The vehicle, or liquid medium.*** This must be an oil which will dry rapidly and harden in drying to a more or less flexible, hornlike body. These changes in the oil are due to oxidation by the air. A number of different oils will serve this purpose, but linseed oil has long been used as the standard drying oil, since it can be produced in quantity and at moderate cost. It is customary to add to it a *dryer*, made by boiling some of the oil with oxides of manganese, lead, or cobalt. The oxides enter into combination with the oil and assist catalytically in its oxidation.

2. ***The body.*** The body of the paint must be some solid material, suspended in the oil, which will give a smooth and waxy surface as the paint dries, and will have good covering power. While white lead meets these requirements, it is moderately expensive and it also blackens when exposed to hydrogen sulfide, which is likely to be present in the air in cities. Other bodies are now frequently combined with the lead, or replace it altogether, among them being zinc oxide, China clay (or kaolin), barium sulfate, and a product called lithopone (p. 320). For some

purposes these materials are a real advantage, and they are not to be regarded as adulterants unless sold as white lead.

3. ***The pigment, or coloring matter.*** In the case of white paints the body serves also as the coloring matter. For other colors a specific pigment must be added. In most cases these pigments are metallic oxides or salts, and are frequently natural products. Sometimes they are prepared by precipitating an amorphous body (usually a colloid) in the presence of an organic dye, the dye being absorbed by the precipitate and giving it a color. Such pigments can be prepared in endless variety of colors, and are called *lakes.* They are usually not so permanent as mineral pigments.

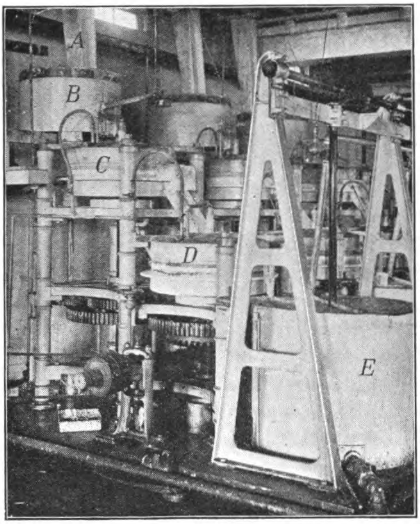


FIG. 181. Apparatus used in grinding and mixing paints

Fig. 181 represents the method of manufacture of paint. The body, together with a little oil, enters at *A* and is ground in succession in *B*, *C*, *D*, and *E*, during which process the requisite amounts of oil, dryer, and pigment are added.

OTHER IMPORTANT COMPOUNDS OF LEAD

Lead nitrate ($Pb(NO_3)_2$): white soluble crystals

Lead chloride ($PbCl_2$): white needles, very sparingly soluble

Lead sulfate ($PbSO_4$): an insoluble white crystalline powder

Lead acetate ($Pb(C_2H_3O_2)_2 \cdot 3\,H_2O$): a soluble white salt called *sugar of lead*

Lead chromate ($PbCrO_4$): used as a pigment in paint (*chrome yellow*)

EXERCISES

1. How could you detect lead if it were present in tin foil?

2. Stannous chloride reduces gold chloride ($AuCl_3$) to gold. Give equation.

3. What are the products of hydrolysis when stannic chloride is used as a mordant?

4. How could you detect arsenic or copper in lead?

5. In obtaining stannic chloride from scrap tin plate the product is contaminated with ferric chloride. Can you suggest a way to purify it?

6. What sulfates other than lead are insoluble?

7. Could lead nitrate be used in place of barium chloride in testing for sulfates?

8. The purity of white lead is usually determined by observing the weight of carbon dioxide given off when it is treated with an acid. On the supposition that it has the formula $(PbCO_3)_2 \cdot Pb(OH)_2$, how nearly pure was the sample if 1 g. gave 102.1 mg. of carbon dioxide? *Ans.* 90% pure.

9. Silicon belongs in the same family with tin and lead. In what respects are these elements similar?

10. What reaction would you expect to take place when lead peroxide is treated with hydrochloric acid?

11. What weight of tin could be obtained by the reduction of 1 ton of cassiterite? *Ans.* 1576 lb.

12. White lead is often adulterated with barite. Suggest a method for detecting it, if present, in a given specimen of white lead.

TOPICS FOR THEMES

The lead mines of Missouri (Geological Reports, Washington Bureau of Mines).

Tin mining in Cornwall (see encyclopedia).

How shot is made (see encyclopedia).

CHAPTER XXXIX

URANIUM AND RADIUM

Uranium. Uranium is a rare element whose compounds were first isolated from a mineral called *pitchblende* or uraninite, which is essentially an oxide of the formula U_3O_8. *Carnotite*, a mineral discovered more recently (1899), contains both uranium and vanadium, and is found chiefly in Colorado and Utah. The carnotite ores are by far the most abundant source of uranium, the next in importance being the pitchblende deposits in Austria, owned by the government. The American production of uranium ores in 1912 amounted to over twice as much as that of all other countries combined.

Compounds and uses. The most familiar compounds of uranium are the black oxide, U_3O_8, and the yellow uranyl nitrate, $UO_2(NO_3)_2$. Most of the compounds of uranium are yellow or red. Their chief chemical use is in making greenish-yellow fluorescent glass, in the decorating of china with various shades of yellow, orange, and black, and in the making of orange-colored pigments. Uranium steel alloy has useful properties.

Radioactivity of uranium. In 1896 the French physicist Becquerel discovered that uranium and all its compounds possess a property which has been named *radioactivity.* This radioactivity manifests itself in the following ways: (1) A photographic plate wrapped in black paper and placed near a compound of uranium is affected as though exposed to light. A metallic object placed on the plate screens the plate from this action, and leaves its outline on the plate when it is developed, forming a *radiograph* (Fig. 182). (2) A charged electroscope is rapidly discharged when any material containing uranium is brought near it, showing that the air all about this material is an electrical conductor.

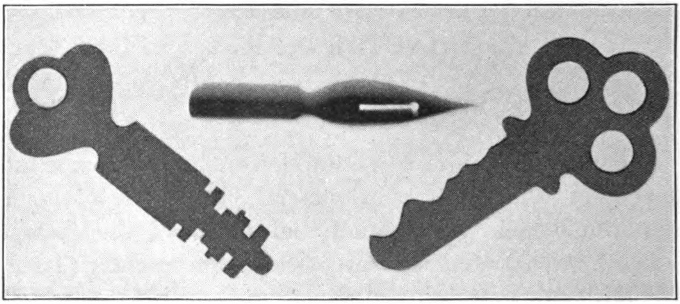


Fig. 182. A radiograph of some metal objects

Fig. 183 represents a simple form of aluminium-leaf electroscope, the leaves assuming the position indicated at *B* when an electric charge is communicated to the knob *A*. When a substance containing uranium (Fig. 184, *C*) is brought near the knob, the charge is rapidly lost, and the leaves collapse as shown at *B*.

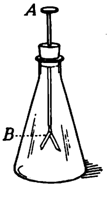


Fig. 183. An electroscope

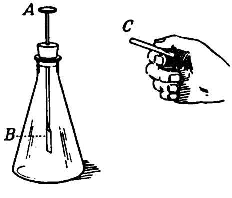


Fig. 184. Discharging an electroscope

The discovery of radium. Pitchblende was found to be 4 times as radioactive as uranium itself, which suggested that possibly there was some unknown element in the mineral that was carried over into the uranium salts as an impurity and was responsible for the radioactivity. Accordingly Monsieur and Madame Curie worked over the residues from a very large quantity of pitchblende, and obtained a minute quantity of the chloride of a new element, which was named *radium.* This chloride is about 3,000,000 times as active as uranium.

The atomic weight of radium is 226.4, and this weight, as well as all of the other properties of the element and of its compounds, place it in the calcium family, just below barium. The metal itself was isolated by Madame Curie (Fig. 185) in 1910, and is very similar to barium.

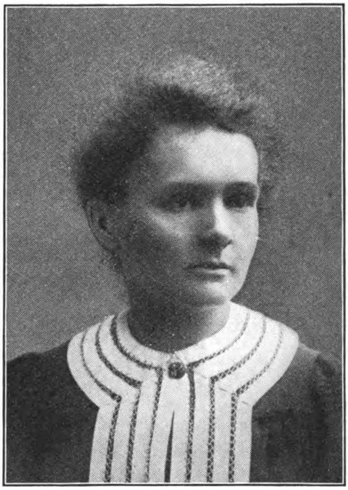


FIG. 185. Madame Curie (1867–)

Professor of Physics in the University of Paris

Quantity of radium available. Knowing the radioactivity of both uranium and radium, it is not difficult to estimate the proportion of radium in any ore containing uranium. Estimates of this kind bring to light a very surprising fact — the proportion of radium in all classes of uranium ores *is very constant*, and is about 1 part of radium in 2,940,000 parts of uranium.

During 1914 there was produced in the United States 87 tons of uranium oxide, and at the ratio just given this should yield 29.4 g. of radium chloride. The total production from foreign ore in 1912 was less than 4 g. Probably the total quantity produced up to 1914 is less than 50 g. The present price of the chloride is about $90,000 per gram.

Disintegration of radium. The extraordinary fact about radium is that although it is a well-characterized element, it is *slowly disintegrating.* In this process it is resolved into two other elements, one of which is *helium* and the other *niton.* These both belong in periodic Group 0 with the inactive gases of the atmosphere. Niton, in turn, decomposes into helium and still another element named radium A. Similar decompositions continue through a number of stages, and it is thought that the final product is *lead.*

In these decompositions two distinct kinds of particles are shot off with enormous velocity: (1) the one kind, called *alpha* rays, consists of helium atoms charged positively and moving with a velocity about $\frac{1}{10}$ that of light; the other, called *beta* rays, consists of particles not more than $\frac{1}{1700}$ of the weight of a hydrogen atom and negatively charged. These are usually called *electrons*, and their initial velocity is nearly that of light. The rate at which this decomposition proceeds cannot be changed by any means that has yet been tried. It is not affected by very high temperature nor by the nature of the radium compound.

Origin of radium. Radium is decomposing at a rate which places its average life at 2500 years, yet it is found in ores which are undoubtedly much older than this. It must therefore be in the process of formation from some other element. Experiment leaves no doubt that this element is *uranium.* The quantity of radium so constantly present in ores of uranium simply represents the equilibrium between the rate at which uranium disintegrates and that at which radium disintegrates. If this is the case, it is clear that we can never hope to find any deposits of radium richer than those afforded by uranium ores.

Energy of radium. During the decomposition of radium, niton, and the succeeding products, a very great deal of energy is given off. Both the helium atoms and the electrons are shot off with very high kinetic energy, and the radium compound is kept heated by the heat energy set free. It is estimated that 1 gram of radium *hourly* evolves 132 calories of heat. From this value, together with the average life period (2500 years), it is easy to compute that the *total* energy given off by a gram of radium will be 250,000 times the heat of combustion of a gram of carbon. These unquestioned facts have thrown a great deal of doubt upon the older estimates of the age of the earth.

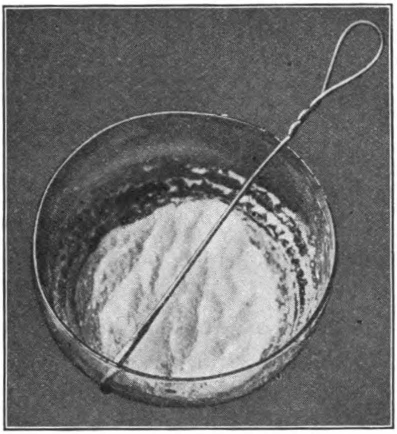


FIG. 186. Total amount of radium bromide (1.764 g.) extracted from 300 tons of carnotite (actual size)

Radium and the atomic conception. It is clear that the atom of radium, as well as that of uranium, must have a very elaborate structure, since helium, electrons, and free energy are formed from them. There is good reason for thinking that *all* atoms have a somewhat similar structure — a little like a miniature solar system; but other atomic systems do not disintegrate like the ones we have been considering.

Radium and medicine. The rays emitted from radium, niton, and other radioactive elements produce many chemical and physiological effects. They disintegrate glass, water, and many other substances. They produce severe burns upon the skin, like those of X rays. They kill bacteria and other microörganisms.

This latter property has led to the hope that exposure to the radiations of radium compounds might prove to be of assistance in effecting a cure for some diseases of the skin and for cancer. It is not possible as yet to say to what extent these hopes will be realized. Certain forms of cancer have apparently been cured in this way.

Radioactive thorium. The rare element *thorium* exhibits properties very similar to those of uranium. It gives rise to the same kind of a series of radioactive elements by successive decomposition, producing the same varieties of radiation as the other series. Uranium and thorium are the elements of greatest atomic weight, and no others are known to possess similar properties. This suggests the idea that possibly elements of still higher atomic weight may have existed at some time, but that they have disintegrated to form elements of smaller atomic weight which are not radioactive.

EXERCISES

1. When was uranium discovered, and how did it get its name (see encyclopedia)?
2. For whom was carnotite named (see dictionary)?
3. How is an electroscope charged (see physics)?
4. What is the meaning of *alpha* and *beta*?
5. What is the velocity of light (see physics)?
6. How did thorium get its name? For what is the element used?

TOPICS FOR THEMES

The discovery of radium (McPherson and Henderson, Course in General Chemistry).

Radium ores of the United States (Bureau of Mines, Washington, D.C.).

Radium in medicine. (See current magazines.)

CHAPTER XL

MANGANESE AND CHROMIUM

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	FORMULAS OF ACIDS
Manganese	Mn	54.93	7.39	1260°	H_2MnO_4 and $HMnO_4$
Chromium	Cr	52.	6.50	1520°	H_2CrO_4 and $H_2Cr_2O_7$

MANGANESE

Occurrence. Manganese is found in nature chiefly as the dioxide MnO_2, called *pyrolusite.* In smaller amounts it occurs as the oxides Mn_2O_3 and Mn_3O_4, and as the carbonate $MnCO_3$. Some iron ores also contain manganese.

Preparation and properties. The metal is difficult to prepare in pure condition, and has no commercial applications. It somewhat resembles iron in appearance, but is harder, more fusible, and more readily acted upon by air and moisture. Acids readily dissolve it, forming *manganous* salts. An alloy of manganese and iron, called *ferromanganese,* is made by reducing a mixture of oxides of the two metals, and is used in the steel industry.

Manganese dioxide (pyrolusite) (MnO_2). This substance is the ore from which all other compounds of manganese are made. It is a hard, brittle, black substance which is valuable as an oxidizing agent. It will be recalled that it has been used in the preparation of chlorine and oxygen, and in decolorizing glass which contains iron. At present its chief use is in the manufacture of ferromanganese.

Manganous salts. Manganese acts as a *bivalent metal*, forming a series of salts with all the common acids. The chloride and the sulfate may be prepared by heating the dioxide with hydrochloric acid and sulfuric acid respectively. The sulfide, carbonate, and hydroxide, being insoluble, may be prepared from a solution of the chloride or sulfate by precipitation with the appropriate reagents. Most of the manganous salts are pink. They not only have formulas similar to the *ferrous* salts but resemble them in many of their chemical properties.

The formulas of some of these salts are as follows:

Manganous chloride	$MnCl_2 \cdot 4\,H_2O$
Manganous sulfide	MnS
Manganous sulfate	$MnSO_4 \cdot 4\,H_2O$
Manganous carbonate	$MnCO_3$

Potassium permanganate ($KMnO_4$). When manganese dioxide is fused with potassium hydroxide and an oxidizing agent, and the resulting mass is extracted with water, a deep-green solution is obtained. This color changes to a very intense reddish purple when carbon dioxide is passed into the solution, and upon evaporating, purple-black crystals of *potassium permanganate* ($KMnO_4$) are formed. This is the potassium salt of *permanganic acid* ($HMnO_4$). The free acid gives a solution of the same intense color as do all permanganates.

Oxidizing properties of potassium permanganate. Potassium permanganate is remarkable for its strong oxidizing properties, especially in the presence of an acid. When sulfuric acid is present, the reaction takes place in such a way that *both the potassium and the manganese are changed into sulfates*, with the liberation of oxygen, as shown in the equation

$$2\,KMnO_4 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,[O]$$

Under ordinary conditions, however, the reaction does not take place except in the presence of a third substance which is capable of oxidation. The oxygen is not given off in the free state, but is used up in effecting oxidation. This is indicated by inclosing its symbol in brackets.

Chromium

Occurrence. The ore from which all chromium compounds are made is *chromite*, or chrome iron ore ($FeCr_2O_4$). This is found most abundantly in New Caledonia, Greece, and California. The element also occurs in small quantities in many other minerals.

Preparation and properties. Chromium, like manganese, is very hard to reduce from its ores, owing to its great affinity for oxygen. It can be produced by the Goldschmidt method (p. 325). The pure metal has no commercial uses, but an alloy of chromium with iron, called *ferrochromium*, is used in the steel industry. Chromium is a very hard metal of about the same density as iron.

Chromic hydroxide ($Cr(OH)_3$). This substance, being insoluble, can be obtained by precipitating a solution of the chloride or the sulfate with a soluble hydroxide. It is a greenish substance which, like aluminium hydroxide, dissolves in excess of alkalies. Both the hydroxide and the corresponding oxide, Cr_2O_3, are used as green pigments.

Chromic salts. Chromium acts as a *trivalent* metal, forming a series of salts resembling *ferric* salts in formula. Most of them are green or violet in color. The most important of the chromic series are the following:

Chromic chloride	$CrCl_3 \cdot 6\,H_2O$
Chromic sulfate	$Cr_2(SO_4)_3$
Potassium chrome alum	$KCr(SO_4)_2 \cdot 12\,H_2O$

A number of the salts of chromium are used in the dyeing industry, for they hydrolyze like aluminium salts, and the hydroxide forms a good mordant.

Potassium chromate (K_2CrO_4). When a chromium compound is fused with potassium hydroxide and an oxidizing agent, potassium chromate (K_2CrO_4) is formed. With chromium hydroxide the equation is as follows:

$$2\,Cr(OH)_3 + 4\,KOH + 3\,[O] \longrightarrow 2\,K_2CrO_4 + 5\,H_2O$$

Properties of chromates. The chromates are salts of the unstable *chromic acid* (H_2CrO_4), and as a rule are yellow in color. Most of the chromates are insoluble, and can be prepared from the soluble potassium salt by precipitation. In the case of lead chromate the equation is as follows:

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2\,KNO_3$$

Lead chromate (chrome yellow) and barium chromate are used as yellow pigments.

Potassium dichromate ($K_2Cr_2O_7$). When potassium chromate is treated with sulfuric acid, the potassium salt of *dichromic acid* ($H_2Cr_2O_7$) is formed:

$$2\,K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

This is the best-known dichromate, and is the most familiar chromium compound. It forms large crystals of a brilliant-red color, and is rather sparingly soluble in water. Potassium dichromate finds use in many industries as an oxidizing agent, especially in the preparation of organic substances, such as the dye *alizarin*, and in the construction of several kinds of electrical batteries.

Leather. Leather is made from the skins of various animals, the processes employed being such as to make the material pliant, impervious to water, and not subject to putrefaction.

The hair is removed by treatment with milk of lime, and the skin is then washed with dilute acid to neutralize the lime and cause the skin to swell. It is then soaked in some *tanning* solution, the active reagent of which combines with the nitrogenous constituents of the skin and changes them into substances which do not decay. Formerly the bark of hemlock and oak trees, which contain *tannin*, was exclusively used for this purpose, but more recently potassium dichromate is often used, as by this method the time required for tanning is much shortened. Finally, the tanned skin is treated with oil to make it soft and waterproof.

Oxidizing action of potassium dichromate. When a dilute solution of potassium dichromate is treated with sulfuric acid, no reaction apparently takes place. However, if there is present a third substance capable of oxidation, the dichromate gives up a portion of its oxygen to this substance, and both the potassium and the chromium are converted into sulfates. The oxidation of ferrous sulfate by potassium dichromate is a good illustration, the reaction being represented in two steps:

$$K_2Cr_2O_7 + 4\,H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3\,[O]$$

$$6\,FeSO_4 + 3\,H_2SO_4 + 3\,[O] \longrightarrow 3\,Fe_2(SO_4)_3 + 3\,H_2O$$

This reaction is often employed in the analysis of iron in iron ores.

EXERCISES

1. How does pyrolusite effect the decolorizing of glass containing iron?

2. Write the equations for the preparation of manganous nitrate, manganous carbonate, and manganous hydroxide.

3. Write the equations representing the reactions which take place when ferrous sulfate is oxidized to ferric sulfate by potassium permanganate in the presence of sulfuric acid.

4. Potassium permanganate is sometimes injected as a cure around the wound caused by a rattlesnake bite. How would you suppose it acts?

5. Where is New Caledonia?

6. Why do all permanganates have the same color in solution?

7. 10 g. of iron was dissolved in sulfuric acid and oxidized to ferric sulfate by potassium permanganate. What weight of the permanganate was required? *Ans.* 5.66 g.

8. Potassium chromate oxidizes hydrochloric acid, forming chlorine. Write the complete equation.

9. 20 lb. of ferrochromium containing 40% chromium was added to a ton of steel. What per cent of chromium did the product contain? *Ans.* 0.398.

TOPICS FOR THEMES

The alums (see encyclopedia).

How sole leather is made (Lassar-Cohn, Chemistry in Daily Life).

CHAPTER XLI

PLATINUM AND GOLD

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	HIGHEST OXIDE	HIGHEST CHLORIDE	MELTING POINT
Platinum	Pt	195.2	21.50	PtO_2	$PtCl_4$	1755°
Gold . .	Au	197.2	19.32	Au_2O_3	$AuCl_3$	1062°

PLATINUM

Occurrence. About 90 per cent of the platinum of commerce comes from Russia, small amounts being produced in California, Brazil, and Colombia. Like gold, it usually occurs in metallic grains in heavy sands, but it has recently been found in eastern Germany in combined form.

Preparation. Native platinum is usually alloyed with gold and other rare metals. To separate the platinum, the alloy is dissolved in aqua regia, which converts the platinum into *chloroplatinic acid* (H_2PtCl_6). Ammonium chloride is then added, which precipitates the platinum as insoluble ammonium chloroplatinate:

$$H_2PtCl_6 + 2\,NH_4Cl \longrightarrow (NH_4)_2PtCl_6 + 2\,HCl$$

On heating the ammonium compound, it is decomposed, leaving the platinum as a powdery metallic mass known as platinum *sponge*. This may be melted into an ingot in an electric furnace and rolled or hammered into any desired shape.

Properties. Platinum is a grayish-white metal of high luster, and is very malleable and ductile. It melts in the oxyhydrogen blowpipe and in the electric furnace, and is a good conductor of electricity. In finely divided form it has the ability to absorb, or *occlude*, gases, especially oxygen and hydrogen. These gases, when occluded, are in a very active condition resembling the nascent state, and can combine with each other at ordinary temperatures. A jet of hydrogen or coal gas directed upon spongy platinum quickly ignites.

Platinum as a catalytic agent. Platinum is remarkable for its property of acting as a catalytic agent in a large number of chemical reactions, and mention has been made of this use of the metal in connection with the manufacture of sulfuric acid. When desired for this purpose some porous or fibrous substance, such as asbestos, is soaked in a solution of chloroplatinic acid and then ignited. The platinum compound is decomposed and the platinum deposited in very finely divided form. Asbestos prepared in this way is called *platinized asbestos*. The catalytic action seems to be in part connected with the property of absorbing gases and rendering them nascent. Some other metals possess this same power, notably palladium, which is remarkable for its ability to absorb hydrogen.

Chemical conduct. Platinum is a very inactive element chemically, and is not attacked by any of the common acids. Aqua regia slowly dissolves it, and it is also attacked by fused alkalies. It combines at higher temperatures with carbon and phosphorus, and forms alloys with many metals. It is readily attacked by chlorine but not by oxidizing agents.

Applications. Platinum is very valuable as a material for the manufacture of chemical utensils which are required to stand a high temperature or the action of strong reagents.

Platinum crucibles, dishes, forceps, electrodes, and similar articles (Fig. 187) are indispensable in the chemical laboratory. In the industries platinum is used for such purposes as the manufacture of pans for evaporating sulfuric acid, and wires for sealing through incandescent-light bulbs; and also as a catalytic material in a number of reactions, and for making a great variety of instruments. A large fraction of the annual production is used for jewelry. Unfortunately the supply of the metal is very limited, and its cost is steadily advancing, so that it is now more valuable than gold.

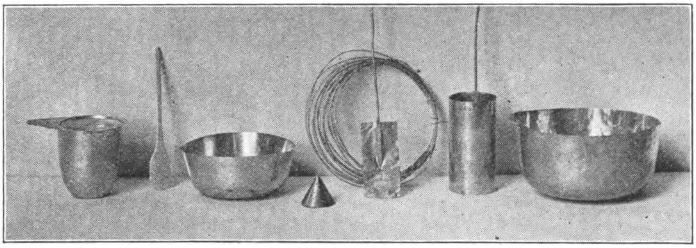


FIG. 187. Some laboratory utensils made of platinum

Chloroplatinic acid (H_2PtCl_6). When platinum is dissolved in aqua regia and the solution is evaporated to dryness, orange-colored crystals of chloroplatinic acid (H_2PtCl_6) are obtained. The potassium and ammonium salts of this acid are nearly insoluble in water and alcohol.

GOLD

Occurrence. Gold has been found in many localities, the best known being South Africa, Australia, Russia, and the United States. In this country it is found in Alaska and in nearly half of the states of the union, notably in California, Colorado, and Nevada. It is usually found in the native condition, frequently alloyed with silver; in combination it is sometimes found as telluride ($AuTe_2$). The United States produces over one fifth of the world's annual output.

Extraction. The extraction of gold is accomplished in a number of ways, according to the character of the deposit. In placer mining the gold-bearing sand is washed by a current of water which is so regulated that particles of light weight are swept away, while the heavier gold is obtained as a sediment. In hydraulic mining the earth and sand are swept into sluices by powerful streams of water operated by pumps. In quartz mining the quartz is stamped to powder and is then washed over copper plates, the surfaces of which have been amalgamated. The particles of gold stick to the mercury or dissolve in it, the gold being recovered by distillation. In other cases, especially when the gold is in very fine powder or in chemical combination, chemical reactions are employed. In the cyanide process the gold-bearing material is treated with a dilute solution of potassium cyanide, with free access of air. The gold dissolves to form a complex cyanide, from which it can be precipitated by metallic zinc or by electrolysis.

In the chlorination process the ore is treated with chlorine, which converts the gold into the soluble trichloride $AuCl_3$. It is recovered from this solution by suitable precipitants. The treatment of lead and silver ores containing gold, as well as the separation of gold from silver, has already been described (p. 373).

Properties. Gold is a very heavy bright-yellow metal, exceedingly malleable and ductile, and a good conductor of electricity. Its melting point (1062°) is much below that of platinum. It is quite soft, and is usually alloyed with copper or silver to give it the hardness required for most practical uses. The degree of fineness is expressed in terms of *carats*, pure gold being 24 carats; the gold used for jewelry is usually 18 carats, 18 parts being gold and 6 parts copper or silver. Gold coinage is 90 per cent gold and 10 per cent copper.

Chemical conduct. Gold is not attacked by any one of the common acids; aqua regia easily dissolves it, forming *chlorauric acid* ($HAuCl_4$). Fused alkalies also attack it. Most oxidizing agents are without action upon it, and in general it is not an active element.

EXERCISES

1. What is the derivation of the word *platinum*?
2. The "platinum chloride" of the laboratory is made by dissolving platinum in aqua regia. What is this compound?
3. What properties would wire need to have in order to be adapted to sealing through electric-light bulbs?
4. Since gold is cheaper, why is it not used instead of platinum for laboratory utensils?
5. How could gold be precipitated from the chloride?

TOPICS FOR THEMES

Discovery of gold in California (see encyclopedia).
The Alaska gold fields (U. S. Geological Survey, Washington, D. C.).
The uses of platinum (see encyclopedia).

CHAPTER XLII

SOME APPLICATIONS OF RARER ELEMENTS

Rarer elements. A large number of elements are known which have not been described in the foregoing pages because an acquaintance with them is not at all necessary for an understanding of the principles of chemistry.

Some of these, while comparatively rare, could be produced in considerable quantities if there were any commercial use for them. A good example is *tellurium*, an element in the sulfur family obtained as a by-product in copper refining. Others of these elements are so rare that the cost of production is prohibitive, even though they have very useful properties.

Application in the industries. Some of these less familiar elements or their compounds have properties which make them valuable for special purposes, and mention of a few of these applications will be of interest.

The rare earths constitute a group of about sixteen elements, all trivalent and resembling aluminium in a general way. They are very difficult to separate from each other and always occur together in nature. Very large quantities of a mixture of them accumulate in the extraction of *thorium* from monazite sand (p. 213). The only one whose compounds are obtained pure rather easily is *cerium*. Compounds of cerium are used as mordants, as catalytic agents, and in medicine and photography. An alloy of cerium with iron is used as a gas or cigar lighter, since it gives off a stream of sparks when scratched by hard iron.

Thorium oxide, mixed with 1 per cent of cerium oxide, constitutes the material of which most gas mantles are made (Fig. 101).

Titanium in the silicon family is not a very rare element, occurring chiefly as the oxide TiO_2, called *rutile*, and as a constituent of certain iron ores (*ilmenite*). Large quantities of nearly pure titanium or of ferrotitanium are used in making steel rails designed to stand very heavy wear (railway curves and terminals). Titanium oxide is also incorporated in electric-arc carbons (*flaming* arc). Carbons thus made give a more diffused and efficient light than those made from pure carbon. The oxide is also used to impart a yellow color to porcelain and to artificial teeth.

Vanadium also occurs in considerable quantities in carnotite (p. 379) and in certain sulfides found in Peru. It is found as oxide in the ash of nearly all anthracite coal. Ferrovanadium, like ferrotitanium, is used in producing special grades of steel, particularly when great toughness is desired (automobile parts). Its compounds are used as photographic developers, as catalytic reagents in the dye industry (aniline black), as coloring materials in glass, and as mordants.

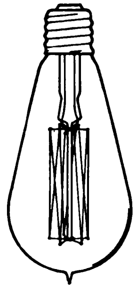


FIG. 188. A tungsten lamp

Molybdenum compounds are used in coloring pottery and in dyeing silk, wool, and leather.

Tungsten compounds are produced in fairly large quantities. It has been found possible to draw the metal into very fine wire (0.3 mm.), which is now extensively used instead of carbon as a filament for incandescent lamps (Fig. 188). Its melting point is very high (3000°), and the consumption of electrical energy for a given candle power is so low that the lamp is about three times as efficient as the older (carbon) lamp. The metal is rapidly replacing platinum for electrical contacts in switches, telephone jacks, and automobile vibrators. Ferrotungsten is used in making steel designed for lathe tools, since such steel can be heated to a red glow without losing temper.

Compounds of tungsten are used for making fireproof cloth, and pigments for paints and pottery, and as mordants.

Selenium, an element in the sulfur family, is obtained as a by-product in refining copper. It is a nonconductor of electricity *when in the dark*, but becomes a fairly good conductor *when exposed to light.* This has led to its use in automatic fire alarms and for regulating automatic gas buoys at sea. Added to glass it produces a fine red color, such glass being used for railway lanterns. It is also used to produce red enamels.

Iridium gives a very hard alloy with platinum, used for pen points, compass bearings, and standard weights and measures.

Palladium is only about half as heavy as platinum, melts much lower, and is harder. It is used as a solder for platinum, for making graduated scales in scientific instruments, and as a substitute for platinum in jewelry. In the form of a powder it is a remarkably active catalytic agent.

APPENDIX

THEME-WRITING IN CHEMISTRY

Following each chapter will be found one or more topics for themes. Much interest will be added to the study of chemistry if the pupil is encouraged to look up for himself some of the details of the lives of the most illustrious chemists and to find out by reading, by consultation, and by observation something more about the applications of chemistry in the arts and industries than can be described in the pages of a brief text. These topics are intended to be merely suggestive. The teacher should add others, especially those concerning which the student will be able to obtain first-hand information.

It is suggested that there should be close coöperation between the teacher of chemistry and the teacher of English. The same theme may be read in the chemistry class for its contents and in the English class for its form. This ought to add interest to both classes without increasing the work of the student and at the same time will emphasize the important fact that the writing of good English should be not merely an exercise for the English classroom but a habit in all written discourse.

If practicable, the student should visit actual plants in operation, and theme topics should be chosen to meet local conditions. Many large firms can supply printed descriptions of their processes and products, and a courteous letter of inquiry is almost certain to bring a courteous reply. It would be well for the teacher to supervise and criticize such a letter to see that it is in proper form and spirit. Printed matter secured in this way should be preserved in available form as the property of the school. Desired information may often be had from a local dealer or agent, and in almost every community there are well-informed persons who would gladly give some time to an inquiring student. Training in the gathering of trustworthy information is far more important than the information itself. The course in chemistry affords unusual opportunities for such training, and it is worth some effort to secure it.

Much that is interesting in regard to the applications of chemistry will be found in the files of various periodicals, such as the *Scientific American*, the *World's Work*, and *School Science and Mathematics*. The bulletins published by the United States Department of Agriculture often contain information of great value to the student of chemistry and they cost but a few cents. A list of available bulletins may be obtained by addressing the Department of Agriculture, Washington, D. C.

A list of books is appended which will be found helpful. The list might easily be greatly extended, but is purposely brief so as to bring it within the reach of almost any high school. In connection with the topics for themes frequent reference is made to the encyclopedia, partly because it is almost sure to be at hand and partly because it is desirable to teach boys and girls to use it freely. Almost any public library will be glad to furnish a list of its books relating to chemical topics, and such a list should be posted in the chemical laboratory.

LIST OF SUPPLEMENTARY BOOKS

ALLYN. Elementary Applied Chemistry. Ginn and Company.
BAILEY. A Textbook of Sanitary and Applied Chemistry. The Macmillan Company.
BIRD. Modern Science Reader. The Macmillan Company.
BLOXAM. Inorganic and Organic Chemistry. P. Blakiston's Son & Co.
DAVY. The Elementary Nature of Chlorine. The University of Chicago Press.
DUNCAN. The Chemistry of Commerce. Harper & Brothers.
DUNCAN. The New Knowledge. Harper & Brothers.
FARADAY. The Liquefaction of Gases. The University of Chicago Press.

FREAR. Breakfast Foods, *Bulletin 162*, Dairy and Food Division, Department of Agriculture, Harrisburg, Pa.

LASSAR-COHN (translated by Muir). Chemistry in Daily Life. H. Grevel Co., London.

MCPHERSON and HENDERSON. A Course in General Chemistry. Ginn and Company.

MARTIN. Triumphs and Wonders of Modern Chemistry. D. Van Nostrand Company.

MUIR. The Story of Alchemy. D. Appleton and Company.

PRIESTLEY. The Discovery of Oxygen, Part I. The University of Chicago Press.

ROGERS and AUBERT. Industrial Chemistry. D. Van Nostrand Company.

ROSCOE and SCHORLEMMER. Inorganic Chemistry, Vols. I and II. The Macmillan Company,

SCHEELE. The Discovery of Oxygen, Part II. The University of Chicago Press.

SCHEELE. The Early History of Chlorine. The University of Chicago Press.

SHERMAN. Chemistry of Food and Nutrition. The Macmillan Company.

STEWART. Chemistry and its Borderland. Longmans, Green, & Co.

THORPE. Essays in Historical Chemistry. The Macmillan Company.

VENABLE. A Short History of Chemistry. D. C. Heath & Co.

WILEY. Foods and their Adulteration. P. Blakiston's Son & Co.

United States Department of Agriculture: (1) Composition of Foods, *Bulletin 28*, Office of Experiment Stations; (2) Nutritive Value of Foods, *Farmers' Bulletin 142*; (3) Some Forms of Food Adulteration and Simple Methods for their Detection, *Bulletin 100*, Bureau of Chemistry; (4) Industrial Alcohol, *Farmers' Bulletins 268* and *269*; (5) Household Tests for the Detection of Oleomargarine and Renovated Butter, *Farmers' Bulletin 231*; (6) The Use of Milk as Food, *Farmers' Bulletin 363*; (7) Canned Fruits, Preserves, and Jellies, *Farmers' Bulletin 203*. (Send to the Department of Agriculture, Washington, D.C., for list of available bulletins, and select such as may be of interest.)

TENSION OF AQUEOUS VAPOR AT VARIOUS TEMPERATURES, EXPRESSED IN MILLIMETERS OF MERCURY

Temperature	Pressure	Temperature	Pressure
0°	4.6	21°	18.62
16°	13.62	22°	19.79
17°	14.4	23°	21.02
18°	15.46	24°	22.32
19°	16.45	25°	23.69
20°	17.51	100°	760.00

WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS, AND BOILING POINTS UNDER PRESSURE OF 760 MILLIMETERS

Name	Weight of 1 Liter	Boiling Point	Name	Weight of 1 Liter	Boiling Point
Acetylene	1.1621	−83.8°	Hydrogen chloride	1.6398	−82.9°
Air	1.2928		Hydrogen fluoride	0.893	+19.4°
Ammonia	0.7708	−33.5°	Hydrogen sulfide	1.5392	−61.6°
Argon	1.7809	−186.0°	Methane	0.7168	−164.0°
Carbon dioxide	1.9768	−78.2°	Nitric oxide	1.3402	−153.0°
Carbon monoxide	1.2504	−190.0°	Nitrogen	1.2507	−195.7°
Chlorine	3.1674	−33.6°	Nitrous oxide	1.9777	−89.8°
Helium	0.1782	−268.7°	Oxygen	1.4290	−182.9°
Hydrogen	0.08987	−252.7°	Sulfur dioxide	2.9266	−10.1°

DENSITIES AND MELTING POINTS OF SOME COMMON ELEMENTS

Name	Density	Melting Point	Name	Density	Melting Point
Aluminium	2.65	658.7°	Magnesium	1.74	651.0°
Antimony	6.52	630.0°	Manganese	7.39	1260.0°
Arsenic	5.73		Mercury	13.56	−38.7°
Bismuth	9.80	271.0°	Nickel	8.9	1452.0°
Calcium	1.55	810.0°	Phosphorus	1.83	44.0°
Carbon, diamond	3.52		Platinum	21.50	1755.0°
Carbon, graphite	2.30	<4000.0°	Potassium	0.862	62.3°
Chromium	6.50	1520.0°	Silicon	2.3	1420.0°
Cobalt	8.6	1478.0°	Silver	10.5	960.5°
Copper	8.93	1083.0°	Sodium	0.97	97.5°
Gold	19.32	1032.0°	Sulfur	2.06	112.8°
Iron	7.86	1530.0°	Tin	7.29	231.9°
Lead	11.37	327.0°	Zinc	7.10	419.4°

SOLUBILITY OF VARIOUS GASES IN WATER

NAME OF GAS	VOLUME ABSORBED AT 0° AND UNDER 760 MM. PRESSURE BY 1 LITER OF WATER
Ammonia	1298.9 liters
Hydrogen chloride	506.0 liters
Sulfur dioxide	79.79 liters
Hydrogen sulfide	4.37 liters
Carbon dioxide	1.713 liters
Oxygen	0.0496 liters
Hydrogen	0.0214 liters
Nitrogen	0.0233 liters

TABLE OF SOLUBILITY OF VARIOUS SOLIDS

SUBSTANCE	FORMULA	WEIGHT DISSOLVED BY 100 CC. OF WATER AT		
		0°	20°	100°
Calcium chloride	$CaCl_2$	59.5 g.	74.5 g.	159.0 g.
Sodium chloride	NaCl	35.70 g.	36.0 g.	39.80 g.
Potassium nitrate	KNO_3	13.30 g.	31.6 g.	246.0 g.
Copper sulfate	$CuSO_4$	14.30 g.	21.7 g.	75.4 g.
Calcium sulfate	$CaSO_4$	0.759 g.	0.203 g.	0.162 g.
Calcium hydroxide	$Ca(OH)_2$	0.185 g.	0.165 g.	0.077 g.

RELATION OF COMMON UNITS AND METRIC UNITS

1 pound (troy) = 373.24 grams
1 pound (avoirdupois) = 453.59 grams
1 ounce (avoirdupois) = 28.35 grams
1 United States quart = 0.946 liters
1 liter = 1.056 United States quarts
1 meter = 39.37 inches
1 centimeter = nearly $\frac{2}{5}$ inch
1 kilogram = nearly $2\frac{1}{5}$ pounds avoirdupois

INDEX

$+Na_2SO_4+2H_2O+Cl_2$