NDUCTIVE
EMISTRY

BRADBURY

CARL WILHELM SCHEELE

B. Sweden, 1742. D. 1786

Discovered oxygen, chlorine, manganese and barium. First prepared arsine and potassium cyanide. Proved that graphite is a form of carbon. Devised a method of obtaining phosphorus from bones.

TWENTIETH CENTURY TEXT-BOOKS

AN
INDUCTIVE CHEMISTRY

BY

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> "De grandes questions restent à résoudre, et cette chimie minérale, que l'on croyait épuisée, n'est qu'à son aurore."
> HENRI MOISSAN.

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PREFACE

In Chemistry, as in other sciences, there are, in the main, two things to be considered—method and results. There is an enormous mass of facts from which we have to select the indispensable things for the beginner, and there is the general procedure or method by which those facts have been ascertained. This book attempts to teach the method of the science along with the facts, and to unify the facts and logically connect them by means of the method. It is hoped that the student who has read it will not only know something about the subject but will know *how* he knows it—that he will be able to give the evidence on which his beliefs are based. The chapter on the atmosphere furnishes a good illustration of the working out of this principle. The composition of the atmosphere is regarded as a problem. A beginning is made by utilizing the information which the student already possesses. This leaves him face to face with questions which can only be answered by experiments. The discussion of these leads to new questions, which suggest other experiments and so on until the desired result it obtained.

Anyone who desires to do so can easily satisfy himself that this plan possesses great advantages over the dogmatic procedure. No originality is claimed for it, for it is simply the inductive method employed by a large and increasing number of teachers. It will be clear that an essential feature of the plan is a constant effort to dovetail the facts of the science with the facts of every-day life in such a way that the student at no time gets the impression that he has attacked something quite foreign to his ordinary experience. Thus, the systematic classification of the elements, which completely determines the order of topics in a work of reference, should only be allowed a subordinate influence upon the arrangement of an elementary text.

The book is not an abbreviated college text, nor a handbook subjected to hydraulic compression. The subject-matter has been regarded from the standpoint of the *student* and nothing has been admitted which does not further, in some way, the orderly development of his ideas. More space than is usual has been given to the practical applications of the subject: at the same time the logical connecting structure which has produced the applications, just as a tree produces its fruit, has not been slighted. Special care has been taken to bring the technology abreast of modern practice.

However, a book may be thoroughly modern and exact, on the purely scientific side, and yet prove a complete failure in the classroom, because it is not fitted to the needs of the student. It does the student less damage to put into his hands a clear account of the chemistry of two or three decades ago than to give him an absolutely modern book which he cannot comprehend. There is but one certain method of avoiding the danger of becoming unintelligible to the beginner, namely, to try out every chapter over and over again with average classes, and continually recast the material until all obscurities and defects are eliminated. This has been done thoroughly with the present book, and I have made quite sure that there is nothing in it which is not easily within the comprehension of the average student beginning the subject.

The plan of beginning with sulphur, the familiar metals and their sulphides originated with Ohmann. There can be no question that this order of topics has many advantages over the usual method of starting with hydrogen and oxygen. The beginner has yet to acquire the conception of a gaseous substance. The foundations of the subject can be laid far more securely when the early part of the work is concerned entirely with familiar solids.

The oxygen basis has been adopted for the atomic weights. Since the hydrogen standard is now entirely obsolete, it is no longer permissible to teach it. Experience has shown that the difficulties in elementary instruction, which were apprehended at the time the change to the oxygen standard was made, have not materialized.

A text-book is hardly an original piece of work. I have drawn freely upon the literature of the science, but there are two authors to whom I am under special obligations, Otto Ohmann and Alexander Smith. Chemists are to be congratulated upon the fact that each of these gentlemen has thought it worth while to devote to the complex problems of elementary chemical instruction the powers of a penetrating intelligence of the first order.

The book covers thoroughly the various requirements and syllabi which teachers preparing students for college have to consider.

I am indebted to Dr. Harry F. Keller, of the Philadelphia Central High School, and to Dr. David W. Horn, of the Philadelphia Central Manual Training High School, for most careful critical readings of the manuscript and for many valuable suggestions. My thanks are due to Dr. Keller, also, for lending me the plates from which the portraits were made. Prof. Shelley and Prof. Morris of the Southern High School have assisted me in the reading of the proof.

Most of the illustrations are from original drawings made by my wife. The remainder have been taken from various sources.

I hardly imagine that the teacher who will give the book a careful reading will conclude that any part of it is "too difficult for the beginner," although it is likely that no text-book has ever been written of which this statement has not been made. Let me repeat that this is a question of fact which is to be decided not by *a priori* speculation, but by practical class-room work, which, so far as the present book is concerned, has been carefully done.

ROBERT H. BRADBURY.

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BOOK I

SULPHUR AND ITS COMPOUNDS WITH FAMILIAR METALS.—FAMILIAR ELEMENTS WHICH OCCUR IN THE FREE STATE IN NATURE

INTRODUCTION

More than a thousand different materials are found in the earth's crust. They are called **minerals.** Most of them have, by the searching methods of chemistry, been separated into two or more simpler materials. *Lead-glance,* the chief ore of lead, can be separated into lead and sulphur, the common yellow mineral *pyrite* into iron and sulphur, and so on. But a few minerals, like the sulphur, gold and silver of nature, have resisted all attempts to separate them.

Materials which do not yield to this separating or *analyzing* process are called **elements.** We shall begin our study of chemistry with the element **sulphur,** which, in many respects, forms a suitable starting-point. The study of sulphur will lead naturally to that of some important ores like lead-glance, copper-glance and silver-glance, each of which can be separated into two materials, one of which is sulphur and the other the metal from which the mineral is named and on which its value as an ore depends. Leaving sulphur, we shall inquire what other important materials are found as *elements* in nature, and the concluding chapters of the first book will be devoted to the atmosphere, which we shall find to be a mixture of elements.

CHAPTER I

SULPHUR

1. Sulphur Crystals.—Sulphur is often found, near volcanoes, as a dull yellow crust upon the rocks. Less often it occurs in beautiful, transparent, solid masses which have somewhat the shape shown in Fig. 1. These masses are bounded by plane surfaces and are sometimes very perfect in shape, except where they are attached to the rock. At first sight it might seem that they had been given this form artificially, by some operation similar to that by which cut-glass objects or gems are shaped. But they are entirely natural, and the most perfect specimens are formed when the sulphur particles have had opportunity and time to arrange themselves without being interfered with in any way. They are called **crystals** of sulphur.

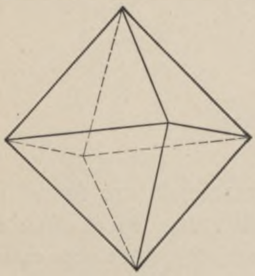

FIG. 1.—Sulphur crystal as found in nature. Simplest form.

A crystal is a natural solid, bounded by plane surfaces. Materials which occur as crystals are said to be **crystallized** or **crystalline.** Materials like glass, rubber and glue, which do not exist in crystalline condition, are said to be **amorphous.**

2. The Production of Sulphur.—Not very long ago, all the sulphur of commerce came from Sicily. Large quantities of it occur there, mixed with limestone, earthy matter and other impurities. It is extracted by piling lumps of sulphur ore into a heap in a shallow pit lined with plaster. The heap is then covered with dust to limit the access of air, and ignited. A smothered burning follows, during which about half the sulphur burns away and the rest is melted by the heat and runs out.

One grave objection to this process can be seen at once. Half the sulphur is wasted. It must not be thought of as de-

LOUIS PASTEUR

B. France, 1822. D. 1895.

Studied fermentation. Investigated the bacteria of the air. Discovered the micro-organism which converts cider into vinegar. Invented the method of "pasteurizing" liquids by gentle heating. Devised the method of inoculation now used to protect against hydrophobia.

stroyed. No material ever ceases to exist. When it disappears it must go *somewhere* and it is usually an easy task to find out what has become of it. In this case the product of the burning of the sulphur passes into the air, where it causes great injury to all forms of plant life, and this is another very bad feature of this method of producing sulphur.

Vast quantities of sulphur were formerly employed in making "oil of vitriol" (sulphuric acid), which is the most important of all chemical products, and is made by the million tons every year (two million in the United States alone). For reasons that we shall understand later, sulphur is no longer employed as the raw material of this great industry.

The United States, which was an important market for the Sicilian product, has begun to produce enough sulphur not only to supply its own needs, but also to export considerable quantities. Workable deposits occur in Nevada, Wyoming and Utah, but, so far, Louisiana has been the chief producer. The method of extraction used in the United States is as follows: Four concentric iron tubes are driven into the sulphur bed. The inner tube is one inch in diameter, the next three, the next six, and the outer tube ten. Through the three-inch tube, water, heated under pressure to a temperature much above the boiling-point, is forced into the deposit to melt the sulphur. Compressed air is driven into the one-inch tube. Melted sulphur, mixed with air, then bubbles up through the outer tubes. The melted sulphur is allowed to run into huge bins, fifty feet high, built of planks, where it solidifies to form a block of practically pure sulphur, which may contain 100,000 tons. This is broken up by blasting, and shipped.

3. Uses of Sulphur.—Sulphur has some important *uses.* Grapevines and fruit trees are subject to the attack of parasites which have devastated orchards and vineyards and led to losses of millions of dollars. *Pasteur* found that finely powdered sulphur, and preparations made from it, are an effective means of destroying these pests. Another use is for the bleaching of *wool*, which is done by hanging the yarn or cloth in a chamber in which sulphur ($\frac{1}{12}$ of the weight of the wool) is burned. *Silk* is often bleached in the same way. *Rubber* is always "vulcanized" before it is fit for any practical purpose. This is a process in which it is made to take up sulphur, 2 or 3 per cent for the soft varieties, and for hard rubber considerably more.

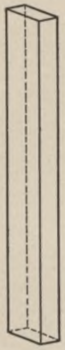

FIG. 2.—Crystal formed by the freezing of melted sulphur.

4. Properties of Sulphur.—There are several different varieties of sulphur. The form whose crystals are found in nature is called α-sulphur (α is the first letter of the Greek alphabet). The roll-sulphur of the laboratory is simply a mass of crystals of α-sulphur.

There is another kind of sulphur which can be made by melting α-sulphur and letting it freeze. We shall call this material β-sulphur (β is the second letter of the Greek alphabet). The shape of the crystals of β-sulphur is shown in Fig. 2. Since β-sulphur changes back to α-sulphur on being preserved, its properties must be determined with a sample freshly prepared.

PROPERTIES [1] OF α-SULPHUR AND β-SULPHUR [2]

	α-SULPHUR	β-SULPHUR
Shape of Crystals	See Fig. 1.	See Fig. 2.
Specific Gravity	2.06	1.96
Melting Temperature	114.5°	119°
Tenacity	Very brittle	Distinctly flexible
Color	Lemon-yellow	Pale honey-yellow
Behavior when preserved at ordinary temperatures	Does not change	Changes to α-sulphur
Behavior when kept at 100°	Changes to β-sulphur	Does not change

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[1] The color, odor, crystalline form of a material, its behavior when heated and acted upon by other substances, etc., are called its *properties*.

[2] All temperatures given in this book are Centigrade.

5. Meaning of the Term "Substance."—The two kinds of sulphur just discussed are quite different and yet they are alike in the fact that they contain sulphur and nothing else. A heap of powdered sulphur presents a different appearance and is suited to different purposes from the same material in a compact roll, and yet, to the chemist, the two are identical. He expresses this by saying that sulphur is a *substance* which can exist in various conditions. Laboratory experience with sulphur will show the student that it may take the form of a liquid, a vapor and at least two different solids. There are, in fact, four or five other solid crystalline modifications which have been studied but which we have no time to consider. Then there is the soft sulphur made in the laboratory, which the student will probably regard as partaking of the nature of both solid and liquid. In just the same way, water is a substance which can take the form of ice (solid), water (liquid), and steam (vapor) under different conditions.

6. Substances are Homogeneous.—It is possible that in the Physical Geography class the student has examined *granite.* A glance is enough to show that there are three things in it and he probably knows that these are the three minerals *quartz, felspar* and *mica.* Granite is not a substance, for it is not **homogeneous.** This means simply that different parts of it are different. The point of a needle can be placed in succession upon three different substances in a block of granite. It is, then, a *mixture* of these three substances. But no different substances can be indicated in a roll of sulphur. It is homogeneous. Chemistry deals chiefly with homogeneous materials, like sulphur and water.

7. More about the Forms of Sulphur.—If the student preserved some of the β-sulphur, which he made by melting roll-sulphur, he must have noticed that each of the needle-like prisms became opaque and brittle, and, at the same time, took on a lemon-yellow color. No doubt this made him suspect that the β-sulphur did not "keep"; that it turned back again to α-sulphur, and, in fact, that is exactly what happened. We have a short way of indicating changes of this kind, thus:

$$\beta\text{-sulphur} \longrightarrow \alpha\text{-sulphur} \quad (1)$$

The arrow may be read "changes to," "produces" or "yields."

Exactly the same thing occurs if a little *soft sulphur* is laid aside. The transparent, elastic threads become opaque, brittle and yellow:

$$\text{Soft sulphur} \longrightarrow \alpha\text{-sulphur.} \quad (2)$$

In this case the change is very slow, and it may be years before it is complete.

The only form which "keeps" is α-sulphur. The other forms all change into α-sulphur when they are preserved at ordinary temperatures. Our science expresses this behavior by the statement that α-sulphur is the **stable** form, or the **natural state** of sulphur. This explains the fact that α-sulphur is the only form found in nature. The others may have been formed, but they could only exist for a short time.

A crystal of α-sulphur will remain for any length of time in the cold, without change of any kind. The sulphur of nature, some of which was produced long before the dawn of history, is a striking proof of this. But α-sulphur, on the other hand, becomes unstable when heated gently. Put a crystal of it in a dry test tube, cork the tube, and surround it with boiling water, and the crystal slowly becomes opaque. Examination with the microscope shows that it has changed to a mass of little prisms of β-sulphur:

$$\alpha\text{-sulphur} \longrightarrow \beta\text{-sulphur} \quad (3)$$

Expressions of the sort given above are called **equations.** Equation (3) is evidently the exact reverse of (1), above. But there is no contradiction, if we remember that (1) takes place only in the cold and (3) only when the sulphur is heated. We can combine the two in one expression:

$$\beta\text{-sulphur} \rightleftarrows \alpha\text{-sulphur} \quad (4),$$

but we must remember to read from left to right if we are thinking about the behavior at ordinary temperatures (1), and from right to left if we mean the behavior at 100° (3).

We can describe the boiling and freezing of water by similar equations. For the boiling we write:

$$\text{Liquid water} \rightleftarrows \text{steam.}$$

We read from left to right for temperatures above the boiling-point (100°), and from right to left for temperatures below the boiling-point. In the same way we can write the freezing of water:

$$\text{Ice} \rightleftarrows \text{Liquid water,}$$

and, recalling the fact that water freezes at 0°, we read from left to right for temperatures above 0° and from right to left for temperatures below.

Related Topics

8. The Melting of Crystalline Substances.—If sulphur is heated and stirred with a thermometer it is found that the instrument registers 114.5° when the sulphur begins to melt and remains at that temperature until the solid is all melted. The *abruptness* of this change should be noted. It takes place sharply at 114.5°, not over a considerable number of degrees as might be expected, and each portion, as it melts, changes at once from a bright yellow, rigid solid to a thin amber liquid, without passing through any pasty or half liquid condition.

In the change of one gram of solid sulphur to liquid sulphur a considerable quantity of *heat* is absorbed. This quantity can easily be measured. It is called the **heat of fusion** of sulphur.

An abrupt passage from solid to liquid at a definite temperature always occurs when a *crystalline* substance melts. Ice behaves in the same way, except that the temperature of melting is

0°. If, in a very cold room (below 0°), we were to fill a test tube with cracked ice, put a thermometer in the ice and heat the tube with a flame, the ice would all remain solid until the temperature was 0° and the thermometer would remain at zero until the ice had all melted. Each second a little of the ice would change from ice (with all the properties of a solid) to water (with the very different properties of a liquid), and there would be no sign of any pasty condition between.

One gram of ice absorbs, in melting, enough heat to warm 80 grams of water through 1° C. This large heat of fusion plays an important part in regulating climate, tending, as it does, to prevent rapid changes of temperature.

9. The Melting of Amorphous Materials.—Very different is the melting of *amorphous* substances. Glass is the best material to experiment with. Hold a rod in the flame. Before it is red-hot it bends and sags, showing that it has begun to melt. The hotter it becomes the more it partakes of the nature of a liquid. It is easy to get it sufficiently liquid to pull out into long threads, but impossible, with the Bunsen flame, to push the heat to the point where the glass becomes a thin liquid.

Glass has no melting-point. From the point where it begins to soften, to the point where it is a liquid as thin as melted sulphur, there is a range of 1000° or more, and in this range there is no particular temperature which can be picked out as the melting-point. It acts, in fact, as though it was at all times a liquid (even in the cold, although then a very stiff one), and simply becomes thinner and thinner the more it is heated. The quantity of heat which is absorbed during the melting of one gram of glass is so small that it has never been measured.

Other amorphous substances, like glue and rubber, behave in the same way. They melt over a range of temperature, and the quantities of heat absorbed in the melting are too small to measure. Crystals are the only *real* solids, and substances like glass, glue and soft sulphur are simply liquids which have become very stiff (*viscous* is the scientific word) by cooling, without ever really becoming solid at all.

10. The Abruptness of Chemical Changes.—When crystals melt, then, they pass, at a definite temperature, from a completely solid state to a completely liquid state, with no intermediate pasty condition to fill the gap. Now all of the changes in matter which form the subject of chemistry are of this singularly abrupt nature. Clean a piece of iron (for instance, a nail) with sandpaper until it is bright, and expose it to the weather for a while. When examined it will be found that it has begun to turn to *rust*, which is red-brown and much less tenacious than iron—easily rubbed to a powder with the hand. There are only two things present; rust, and iron which has not yet had time to turn to rust. We look in vain with a lens, or even a microscope, for any intermediate substance.

Definitions

Crystal. A natural solid, bounded by planes.

Crystalline. Composed of crystals.

Amorphous. Not crystalline.

Homogeneous. Composed of the same material and having the same structure throughout; uniform.

Substance. Any particular homogeneous material; for instance, sulphur, water, sugar or salt.

Mineral. A substance found in the earth's crust.

Ore. A mineral from which some important product, usually a metal, is obtained.

Deposit. A considerable mass of ore or useful mineral.

Viscous. Thick; stiff; sticky; imperfectly liquid.

CHAPTER II

COMPOUNDS OF SULPHUR WITH SOME FAMILIAR METALS

11. Lead-glance, or Galenite.—In many localities in the United States, especially in Missouri, Idaho, Colorado and Utah, occur large quantities of a mineral called *lead-glance* by the miners, and *galenite* by the mineralogists. Its crystals take the form of cubes (Fig. 3), less frequently of octahedrons (Fig. 4), and very often of a combination of both (Fig. 5). Its appearance recalls that of lead, for it has a blue-gray color and a metallic luster, but, although dense (specific gravity 7.6) it is not as dense as lead (specific gravity 11.2). Under the hammer, lead flattens out, but lead-glance is very brittle and breaks always along three planes at right angles to each other, so that the broken mass consists of cubes.

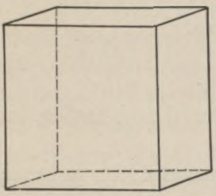
Fig. 3.—Cube.

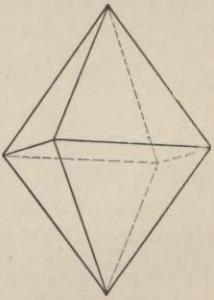
Fig. 4.—Octahedron.

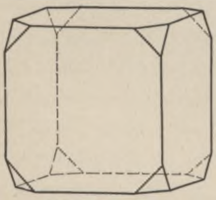
Fig. 5.—Cubo-octahedron.

Lead is readily obtained from galenite. When the mineral is heated on charcoal, with the flame of the blowpipe, a globule of lead is left. At the same time, the sharp odor of burning *sulphur* is perceived. When the powdered mineral is heated with nitric acid, sulphur is formed, and can be identified by its color and by drying and burning it. Nitric acid contains no sulphur, so the latter must come from the galenite.

It seems, then, that it is easy to obtain lead from galenite. Galenite is almost the sole source of the lead of commerce. Sulphur, also, can readily be obtained from it. But, from the pure mineral, nothing but lead and sulphur can be obtained.

The next question that arises is whether galenite can be produced by putting together lead and sulphur. Lead and sulphur are mixed in a test tube and heated. The resulting mass has the properties of lead-glance. There are no large crystals, for the product is formed too quickly, but cubes can be obtained by heating gently for a long time. On charcoal and with nitric acid the artificial product behaves like the galenite of nature. Our conclusion, then, that galenite is composed of lead and sulphur, is based not only on the *analysis* (or taking apart) of the mineral into these two substances, but also on the *synthesis* (or putting together) of lead and sulphur to make it.

12. The Metal from Lead-glance.—*Lead*, the metal which we have obtained from galenite, is softer than gold and not as dense. When freshly cut, it has a bright blue-gray metallic luster, but this is rapidly dimmed by rusting, giving place to the familiar dull gray color of the metal. However, the film of lead rust formed protects the mass beneath and the metal is quite permanent in the air. No doubt the student has noticed that melted lead rusts more rapidly. It becomes covered with a yellow scum called *litharge*, which has no metallic luster and does not resemble lead in the least. By heating long enough all the lead can be converted into this material, which always weighs more than the lead from which it is made. 100 parts by weight of pure lead will always yield 107.7 parts of litharge.

In the same way, when lead and sulphur are heated together to form artificial lead-glance, 100 parts of lead by weight will always form 115.5 parts of lead-glance, taking up 15.5 parts of sulphur. If we use more lead than corresponds to these proportions, the excess of lead remains in the tube, mixed with the lead-glance. On the other hand, if we take too much sulphur, the excess of sulphur is driven off by the heat and escapes in the yellowish smoke which issues from the tube.

13. **Practical Aspects of Lead.**—About a million tons of lead are made in the world each year, of which the United States furnishes about 350,000 tons. Spain and Germany are also important producers.

The metal is plastic when warm and is formed into pipes which are largely used for covering electric cables and in plumbing. **Shot** is made of lead containing a little *arsenic*. **Solder** contains lead and tin. **Type-metal** contains lead, tin and antimony. Lead resists the action of acids and other chemicals better than the other cheap metals and, for that reason, is largely used in practical chemistry. The great chambers in which sulphuric acid is manufactured are made of lead. **"White lead"** and **"red lead"** are no doubt familiar to the student from their extensive use as paints. We shall see that they contain lead, and large quantities of the metal are used in making them. Lead and substances containing it are *poisonous*. Workmen who deal with them are subject to chronic lead poisoning which usually destroys the health in a short time.

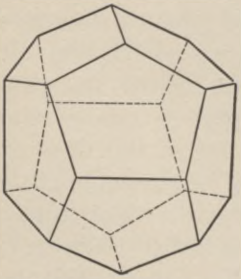

FIG. 6.—Pyrite-crystal.

14. **Pyrite or "Fool's Gold."**—The very common and important mineral, *pyrite*, is yellow, but the color is much lighter than that of gold. It is more like the color of pale brass. Its specific gravity (5) is only about one-fourth that of gold (19). It is readily distinguished from gold by its hardness. It is too hard to be scratched by a knife. Gold is very soft. Like lead-glance, pyrite often crystallizes in cubes or in octahedrons. Another frequent form is

shown in Fig. 6. Pyrite occurs abundantly in many localities. The Rio Tinto mines in Spain have yielded great quantities of it. In the United States it is mined chiefly in Virginia. Most of it goes into the sulphuric acid manufacture. The greater part of the sulphuric acid of commerce is now made from pyrite.

15. Composition of Pyrite.—Now, sulphuric acid, as the name indicates, is a substance containing sulphur, and from the use to which pyrite is put we might suspect that it was rich in sulphur. When the mineral is heated in a glass tube, closed at one end, a yellow ring of sulphur forms in the upper part of the tube. The heated mineral has lost the brass-yellow color of pyrite and has become magnetic. This suggests the presence of *iron.* When some of the powdered mineral is treated with nitric acid, the sulphur is left, just as with lead-glance. Further evidence can be obtained by heating the mineral on charcoal with the blowpipe. The pyrite burns with a blue flame and the sharp odor of burning sulphur is noticed. The substance left on the charcoal betrays the presence of iron by being attracted by a magnet.

16. Iron, the Metal of Pyrite.—*Iron,* the metal contained in pyrite, is white and lustrous when pure and will take a high polish. The commercial forms of iron contain various impurities which have a marked effect upon its strength. The study of the effect of impurities upon iron is a large and important subject. For instance, commercial iron always contains a little sulphur, but if the quantity of sulphur is greater than a few hundredths of one per cent, the iron is so weak as to be worthless.

To mention the uses of iron would be to write an account of modern civilization. About sixty million tons of it are made each year, of which the United States yields nearly one-half. Germany and England are the other great producers. About five-sixths of this enormous quantity is converted into *steel.*

17. Copper Pyrite (Chalcopyrite).—Along with pyrite, often in the same specimen, is found a mineral called *chalcopyrite*, somewhat like pyrite in appearance, but of a deep gold-yellow color. It is much softer than pyrite, and can be easily scratched with a knife. The shape of the crystals (Fig. 7) is quite unlike that of the pyrite crystals.

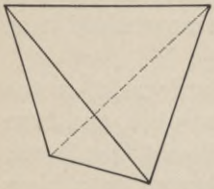

FIG. 7.—A crystal of chalcopyrite.

Heated in a tube sealed at one end, chalcopyrite behaves like pyrite, yielding a ring of sulphur. On charcoal, with the blowpipe flame, it yields a magnetic globule and the odor of burning sulphur. It is clear that sulphur and iron must be contained in it.

When the powdered mineral is treated with nitric acid, it leaves a residue of sulphur, but the liquid over the sulphur is *blue*, which is not the case when pyrite is treated in the same way. If this blue liquid is carefully heated until most of the nitric acid has been driven off and then some water and an iron nail are added, the iron rapidly becomes coated with a red metal which is recognized as *copper*. The copper did not come from the nitric acid, for nitric acid contains no copper. It could not come from the nail. So here is a *third* material obtained from the chalcopyrite. Lead-glance and pyrite can be separated into only *two* substances, but chalcopyrite yields *three*.

Chalcopyrite is an abundant and important copper ore. It occurs at many places in the eastern United States, for instance, near Phoenixville, Pa., and at Ellenville, N. Y., but is most abundant in the West, notably in Montana.

18. Copper.—Copper is rose pink. It can be obtained in leaves so thin as to transmit a green light. It melts much more easily than iron. Pure iron melts only at 1600°, which is far beyond a white heat (1500°). Copper melts at 1100°, which is a yellow heat. Except silver, copper is the best conductor of electricity (and of heat) among the metals.

The metals as a class conduct both heat and electricity very much better than non-metallic materials. Copper is extensively used for wires and cables for conducting the electric current. It must be purified with care, since small amounts of impurities greatly reduce the conducting power. Copper *rust* is green. It is formed more slowly than iron rust, and, like many substances containing copper, is poisonous.

All the iron of the world is obtained from iron ores, that is, substances containing iron. The metal itself scarcely occurs in nature and is nowhere found in sufficient quantities to mine. Most of the copper is obtained from copper ores, like chalcopyrite, but copper *metal*, unlike iron and lead, is found abundantly in some localities. In the copper mines on the shore of Lake Superior, in northern Michigan, masses of the metal weighing hundreds of tons have been found. About 850,000 tons of copper are produced in the world each year, of which the United States furnishes one half. The chief copper-producing states are Montana, Arizona, Michigan and Utah.

The method employed in extracting the copper from chalcopyrite, or some similar method, would show the presence of very small quantities of copper in many materials of the mineral world, and in some animal and plant structures. Thus, traces of it are contained in the red feathers of some birds, in hops, in the human kidneys and in the blood of the cuttlefish, which is blue when arterial, and colorless when venous.

19. Cinnabar.—The mineral *cinnabar* is mined extensively at New Almaden, Cal., at Almaden in Spain and at Idria in southeastern Austria. It is easily distinguished from most other minerals by its red color, its softness, and its high specific gravity (8). Heated on charcoal, it disappears in a gray smoke, giving at the same time the odor of burning sulphur. Heated with a little iron powder, in a test tube, a ring forms in the cooler part of the tube which is seen to consist of small drops of mercury (quicksilver).

It appears, then, that cinnabar contains mercury and sulphur. Synthesis confirms this and makes it unnecessary to search for other constituents. For when sulphur is melted and heated with a little mercury, a substance having all the properties of cinnabar is formed.

20. Mercury.—Mercury is obtained by heating cinnabar in a current of air. The gases are passed through long flues in which the mercury deposits.

Mercury is the only liquid metal. It has a bright white metallic luster and a high specific gravity (13.6). At 357° it boils, passing into a colorless vapor. This vapor is formed slowly in the cold. Mercury, left standing in open vessels, shows a loss in weight which can easily be measured on a good balance. If a piece of gold leaf is suspended from the stopper of a bottle containing mercury, the gold will be slowly whitened by mercury deposited upon it.

Mercury freezes at about –40° to a mass which resembles lead, but is lighter in color. Solid mercury can be beaten out, but the part of the hammer which strikes it must be covered with a leather pad, or the mercury must be wrapped in a cloth, for contact with the steel of the hammer (which of course has the ordinary temperature of the room) will immediately melt it.

Mercury is used, on account of its high specific gravity, for filling barometers. When heated its expansion is very regular, and this makes it an excellent liquid for thermometers. The zinc employed in batteries is rubbed with mercury to prevent it from being acted upon when the battery is not in use. Mercury and substances containing it are *poisonous.* Many materials made from it are used in medicines. The annual production of mercury of the world is about 3000 tons.

21. Sphalerite, or Zinc Blende.—*Zinc blende* occurs abundantly with the lead-glance of Missouri, Wisconsin, Iowa and Illinois. This has caused it to be mistaken for galenite, but zinc blende has a much lower specific gravity. The crystals have a different shape (Fig. 8) and a very different luster. Instead of the marked metallic appearance of lead-glance, zinc blende is usually semi-transparent, and has the luster of a piece of rosin, the *resinous* luster.

Treated with nitric acid, zinc blende leaves a residue of sulphur. On charcoal before the blowpipe the odor of burning sulphur is noticed. No metallic globule is obtained, but a coating forms on the charcoal which is yellow when hot and white when cold. This is composed of a substance with which the student is probably familiar. It is "zinc white," so called because it contains zinc and it is extensively used as a white paint. There is no good way of getting the zinc out of zinc blende in the laboratory, but on a large scale this is easily done and zinc blende is the main source of the zinc of commerce.

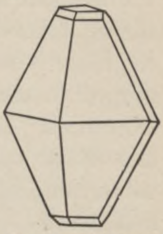

FIG. 8.—A crystal of zinc blende.

When a small quantity of zinc dust is mixed thoroughly on an asbestos plate with about half its weight of finely powdered sulphur, and a flame applied, the mixture burns like gunpowder. A white mass, which is the same substance as zinc blende, is produced. Its appearance is quite different from that of the mineral zinc blende, because it is formed so quickly.

22. Zinc.—Zinc has not been found as metal in nature. It is blue-white, crystalline and, when cold, brittle. At about 130° it becomes malleable and sheet zinc is made by rolling the metal with heated rollers. The sheets retain their flexibility when cold. At a somewhat higher temperature zinc again becomes brittle, and can be powdered in a mortar. It melts at 419° which is below a visible red heat (500°). Somewhat above its melting-point, it takes fire—if the air has access to it—and burns to a loose white powder of *zinc white,* which weighs more than the zinc from which it is obtained. Zinc boils at a bright red heat (930°).

Lead, iron, copper and mercury were known and used by the ancients, but zinc came to Europe from eastern Asia as a curiosity during the

16th century, and has only been important commercially for about a hundred years. The reason can be deduced from laboratory experience. Zinc is more difficult to separate from its ores than the other metals just mentioned. The ancients had no knowledge of chemical science. They only knew the metals which occurred in the free state in nature, like silver and gold, and those which could be very easily obtained from their ores, like lead.

Sheet zinc is used for roofs, gutters and other construction where lightness is important (specific gravity, 7), but its chief use is in "galvanizing" iron. The iron is cleaned and dipped in melted zinc. The object is to protect the iron from rust. The zinc coating serves this purpose better than any other covering. The process is applied to telegraph wires, fencing, sheet iron for building construction, and, in fact, to all iron which is to be exposed to the weather. Even if a small hole forms in the zinc, laying bare the iron, the latter will not rust. The *zinc must rust first,* when iron and zinc are in contact. When iron is plated with tin, the reverse is true. The moment a hole lays bare the iron, the iron begins to rust and the rusting is stimulated by the presence of the tin, which itself stops rusting, being protected by the iron. This is the reason that a roof of tin plate requires frequent painting, while galvanized iron lasts very well without paint.

Upwards of 800,000 tons of zinc are made each year, mostly from zinc blende. The United States and Germany are the chief producers, each yielding about one-third of the world's total.

23. Mixture and Compound.—Let us mix 20 grams of copper filings with 10 grams of finely powdered roll sulphur. We should expect the resulting material to consist of little fragments of copper and of sulphur. That this is really its structure can be seen with a lens or a microscope. The two substances are just as truly separate as when they were in two different bottles. The mixing has merely brought them closer together. The mixture is not *homogeneous,* like sulphur and the sulphur-containing minerals we have just studied. It is like a piece of granite in the respect that certain parts of it differ from other parts in properties.

We can easily prove by experiment that the colorless liquid, *carbon disulphide,* takes up sulphur easily and deposits it again when the liquid dries up. But carbon disulphide has no effect upon copper, as can be shown by shaking up a little of it with some copper filings in a test tube.

24. Separating Mixtures.—We can now predict the action of carbon disulphide upon the mixture we have made. When some of it is shaken up with carbon disulphide in a test tube and the liquid poured off into a dish, copper remains in the test tube. When the liquid in the dish has evaporated a deposit of sulphur crystals is left. In exactly the same way one might separate a mixture of salt and sand by treating it with water. The salt would dissolve and the sand remain.

Another method of separating the mixture of copper and sulphur can be based upon the fact that sulphur (specific gravity, 2) is far lighter than copper (specific gravity, nearly 9). Make a liquid whose specific gravity is greater than 2 and less than 9. Throw some of the mixture into it. The copper sinks and the sulphur floats. This method is largely used by geologists in separating powders consisting of minerals of different specific gravity.

Or, stir up some of the mixture with water. The sulphur remains suspended in the water much longer than the copper, and by pouring off at the right time, a partial separation can be carried out. This method does not work well on a small scale, but is extensively employed for separating various mixtures in practical work, where large quantities are dealt with. We should carefully note the principle of it.

One fact about the mixture is self-evident, and of great importance. *We can make it in any proportions we choose.* We took 20 parts of copper to 10 of sulphur so that the mixture contained:

Copper	66.67 %
Sulphur	33.33 %

but we might as well have taken some other proportion, so far as the making of the mixture was concerned. The composition of a mixture is under the control of the person who makes it.

25. Copper-glance.—Now let us lay aside the mixture for a moment and, as a contrast, examine a *homogeneous* substance composed of copper and sulphur. *Copper-glance* is found at Bristol, Conn., at Butte, Mont., and at many other places, *e. g.* in Siberia and South America. It is black-gray and has a metallic luster. It can be proved to consist of sulphur and copper by the same methods employed in analyzing the other sulphur minerals. But no copper or sulphur can be seen in it. The most powerful microscope shows merely a black-gray, uniform mass.

When copper-glance is powdered and shaken up with carbon disulphide, the powder is unaffected. No sulphur is taken up by the liquid, for, if it is poured off and allowed to evaporate, nothing remains.

When the powder is thrown into a liquid whose specific gravity is higher than that of sulphur, it will all sink; no sulphur appears on the surface. A liquid whose specific gravity was higher than 5.5 (the specific gravity of copper-glance) would make all of the powder float, but there are difficulties in the way of obtaining a suitable liquid.

Nor can any separation of the copper and sulphur be carried out by stirring up the powder with water and pouring it off when partial settling has occurred. Both the portion which settles and that which remains suspended consist of copper-glance. The only difference is that the latter is somewhat more finely powdered than the former.

Whether they come from Connecticut or Montana, from South America or Siberia, the pure crystals of copper-glance always contain the same proportions of copper and sulphur:

Copper 79.87 %
Sulphur 20.13 %

This is a fundamental distinction between copper-glance and our mixture, which could have any composition we saw fit to give it.

26. Synthesis of Copper-glance.—It is easy to transform our mixture of copper and sulphur into artificial copper-glance. Place it in a dry test tube and apply heat to one point. A glow begins here and spreads through the mass. Clearly a change is occurring which gives out much heat. When the action is over, we find in the tube a gray-black mass which is similar to copper-glance in appearance, but without well formed crystals because it has been formed so quickly. The copper and sulphur can be obtained from it again, in the same way as from the mineral. Like the copper-glance, it resists the methods of separation based upon the use of carbon disulphide or upon the difference of specific gravity of copper and sulphur.

It will be seen that there is a profound difference between the state of the copper and the sulphur in the mixture, and the condition of the same two substances in copper-glance. Our science expresses this difference by the statement that copper-glance is a **compound** of copper and sulphur. The other minerals which were analyzed into their constituents, and synthesized from their constituents, were also *compounds* of sulphur with the different metals, lead, iron, copper, mercury and zinc. Using our experience with them as a basis, we can state the distinction between compounds and mixtures as in the table on the following page.

27. Discussion of the Table.—The five statements in column B are true of all compounds without exception. The first four statements in column A apply only to mixtures of powders like the mixture of copper and sulphur or of zinc dust and sulphur. There is a great and important class of mixtures called **solutions,** of which these four statements are not true at all. We shall study them in detail later, but, at present, we need only stir up a spoonful of sugar in a cup of water to have a mixture to which these four distinctions in

DISTINCTIONS BETWEEN MIXTURES AND COMPOUNDS

	A—MIXTURES	B—COMPOUNDS
1 **Appearance**	Not homogeneous	Homogeneous
2 **Separation**	Easy by methods based upon the different physical properties of the constituents	Impossible by methods based upon the physical properties of the constituents
3 **Properties**	Can be calculated from those of the constituents	Have no relation to those of the constituents
4 **Heat-production during formation**	None	Usually much heat given out. Sometimes heat absorbed
5 **Proportions of the constituents**	Can be varied at will	Always the same in the same compound

column A do not apply. For (1) the liquid is *homogeneous,* (2) it can *not* be separated into sugar and water by methods similar to those we employed with the mixture of copper and sulphur, (3) the properties of the sugar are entirely lost,[1] (4) there is a decided disappearance of heat when the water takes up the sugar. Distinction (5) holds good, however, in this as in all similar cases, for we can dissolve little or much sugar in the water up to a certain limit. *Therefore, the constancy of composition of compounds is the great distinction between them and mixtures.* This fact, that the composition

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[1] Very likely the student will object that the *taste* of the sugar remains in the liquid. But there is no such thing as the taste of solid sugar. For it must always dissolve in the saliva before it is tasted and the taste is that of the *solution.*

of the same compound is always the same, is called the **law of definite proportions.**

28. Chemical Change.—The compounds of sulphur with other substances are called **sulphides.** Lead-glance is *lead sulphide;* copper-glance is *copper sulphide;* cinnabar is *mercury sulphide.* When copper and sulphur are heated together they unite to form a new substance, *copper sulphide.* Notice the abruptness of the change. As each portion of the mixture in turn changes to the compound, copper sulphide, the properties of copper and sulphur vanish and the properties of copper sulphide appear. There is no gradual passage from mixture to compound, no intermediate stages can be discovered.

When all the properties alter at once in this abrupt way we call the process a **chemical change.** The experiments in which we made the compounds of sulphur with lead, mercury and zinc were chemical changes. So, also, is the burning of zinc in the air to form zinc white.

29. The Business of Chemistry.—The task of Chemistry is the study of chemical changes. We have proved that copper and sulphur combine to form copper sulphide. The next step is to ascertain what *quantities* of the two substances unite. Weigh a little fine copper wire in a porcelain crucible (Fig. 9) and add about an equal weight of sulphur. Heat the covered crucible to redness and weigh again. The substance in the crucible is now copper sulphide and the gain is the sulphur which has combined with the copper. In this way we could show that about 80 parts of copper combine with about 20 parts of sulphur to form 100 parts of copper sulphide, all by weight.

FIG. 9.—A porcelain crucible.

30. Effect of Heating on the Speed of Chemical Changes.—We had to heat the copper and sulphur to make them combine. This fact gives rise to many questions. For instance, does the change occur at all in the cold or not? Does it begin to occur at some definite temperature, say a red heat? Or does the union go on slowly in the cold, so slowly that we cannot wait for it and therefore apply heat in order to quicken it?

We can easily show that sulphur combines with *silver* in the cold. Place a bit of sulphur in the bowl of a silver spoon and look at it every day or two. A black stain of silver sulphide appears on the spoon, surrounding the sulphur for some distance on all sides. This also proves that sulphur, like mercury, passes into vapor slowly in the cold, for otherwise only the part of the spoon in contact with the lump would be blackened. In a similar way, it could be shown that sulphur acts upon copper slowly in the cold and that the only effect of heating is to quicken the change.

31. **The Elements.**—In the laboratory, we have separated lead-glance into sulphur and lead, cinnabar into sulphur and mercury, zinc blende into sulphur and zinc, pyrite into iron and sulphur and chalcopyrite into iron, copper and sulphur. No one has ever succeeded in splitting up sulphur, lead, mercury, zinc, iron or copper into simpler substances. Just as we have worked with these minerals, so chemists have worked with the other compounds found in the crust of the earth, with the object of separating them into simpler materials. As a result, they have obtained about eighty substances, which resist further separation.

A possible explanation of the failure to split up the elements is that they are in reality *simple* substances. For instance, it is quite possible that sulphur has never been separated because there is really nothing but sulphur in it and there are no simpler materials into which it might be separated. This, however, is a *possibility* merely, and the history of our science warns us to be careful how we make statements that any task will always remain beyond its power. Water and air were regarded for centuries as elements, but the development of chemical methods has shown that the first is a compound and the second a complex mixture.

"Chemistry advances toward its goal by dividing, subdividing, and again subdividing, and we cannot tell what will be the limit of its victories. We cannot be sure that the substances which we call *simple* at present are indeed simple; all we can say is that they are the limits to which chemical analysis has arrived, and that, with our present methods, we are unable to subdivide further." (Lavoisier, 1789.)

32. An **element** is a substance which has not yet been (and perhaps may never be) separated into simpler substances. Or, an element is a substance of which the following statement holds good: When it is completely converted into another substance, the product will weigh more than (or, in rare cases, the same as) the substance before the chemical change. Examples: lead can be converted into lead sulphide, which weighs more than the lead. α-sulphur can be converted into β-sulphur whose weight is the same as that of the α-sulphur. Lead *cannot* be completely converted into a product which weighs *less* than the lead.

A **compound** is a homogeneous form of matter which can be separated into at least two substances, and always yields them in the same proportions by weight.

A **solution** is a homogeneous form of matter which may contain its constituents in any proportions by weight, up to a certain limit. Example: brine, which may contain little or much salt up to the point where the water refuses to take up any more.

A **mechanical mixture** is non-homogeneous matter. It is composed of at least two substances, lying side by side, and may contain these substances in any proportions whatever.

The **law of definite proportions:** The composition of the same compound is always the same. The experiments made to test this law would have detected a variation of less than one part in a million. They have failed to show that there is any variation at all.

In a **chemical change** all the properties of a substance change *at the same time,* abruptly. No gradual transition can be traced. We usually express this by saying that a *new substance* is produced. Hang weights an ounce at a time on a spring balance (scale used for weighing ice, for instance). The spring is pulled out in a perfectly continuous way. Two ounces pull it out twice as much as one; the elongation is *proportional* to the weight applied. None of the other properties of the spring are altered. This is a **physical change.** Innumerable changes of this sort occur and their study is the province of the science of *Physics.* The *rusting* of iron is a *chemical* change (p. 9).

Chemistry is the science whose business it is to study chemical changes. This study includes not only the examination of the products, but also that of the change itself and the study of the influence of pressure and temperature upon it. The name of our science is derived from the ancient Egyptian word Chêmi, which was the name the Egyptians gave to their own country. Our science had its beginning in Egypt and the first laboratories of which records have been found were in the Temples of Isis. Only priests were allowed to enter them. However, the systematic study of chemical changes by means of the balance is comparatively a new thing—only a little more than a century old. During this short time it has proved to be the most important business to which men have ever turned their attention. It has revolutionized the conditions of life, and conferred benefits upon the human race which are quite beyond calculation.

Definitions

Cube. A solid bounded by six squares.

Octahedron. A solid bounded by eight triangles. It is shaped like two four-sided pyramids, placed base to base.

Analysis. The separation of a substance into simpler substances.

Synthesis. The putting together of two or more substances to form a new substance of more complicated composition.

Rust. A lustreless, earthy solid, formed by the action of the air upon a metal.

Galvanize. To coat an iron or steel object with zinc.

Specific Gravity. The quotient obtained by dividing the weight of anything by the weight of an equal volume of water.

Sulphide. A compound of sulphur with one other element.

CHAPTER III

SOME NATIVE METALS

33. Native Elements.—Of the elements which we have studied, lead, iron and zinc are found almost entirely in compounds. Sulphur, mercury and copper are also largely found as compounds, but they also occur as elements (*native*). Are there any other elements which have preserved their separate existence? If so, we may venture the prediction that they have comparatively little tendency to produce compounds with other elements. That is, we may expect them to be *inert* or *inactive,* from a chemical standpoint.

We may add to our list of native elements, the metals *gold, silver* and *platinum.* Silver resembles copper and mercury in being found both native and as compounds with sulphur and other elements. The gold and platinum of commerce are derived mainly from the native elements.

34. Gold.—Gold is found in many places, but abundantly in few. The chief localities are South Africa (the Transvaal), the United States (Colorado, California, Nevada), British Columbia (Klondike), Alaska and Australia (New South Wales, Queensland). The world's production of gold has been increasing for many years. Up to 1850 it averaged only about 27 tons a year. At present it is nearly 700 tons, valued at about $450,000,000. The Transvaal is first in the production of gold, and the United States second, yielding about one-fourth the total production. Australia has furnished the largest nuggets. One, found in 1858, weighed 184 pounds, and another (1869) 190 lbs.

35. Different Kinds of Gold Deposits.—Gold may occur in two ways. (1) It may occur in scales scattered through the gravel and sand of river-beds and valleys. The gold can be obtained by a method, the same in principle as the separation of copper and sulphur, by stirring them with water. The gold (specific gravity 19.3) is far denser than the sand and gravel (specific gravity about 2.5). A regulated washing with water will remove the other materials and leave some of the gold. However, such deposits are worked at present by the *cyanide process.* (See §36.)

Or (2) the gold-scales may be distributed through a compact rock, usually quartz. The rock is crushed to a powder in a "stamp mill" and the powder, mixed to a thin mud with water, flows over a copper plate which has been smeared with mercury. The mercury dissolves the gold. After a time it is scraped off and heated. This drives off the mercury, which is collected and used again, while the gold remains. The mud which has flowed over the copper plate still contains nearly half the gold. This is extracted by the "cyanide process."

36. The Cyanide Process.—*Potassium cyanide* is a white, poisonous solid which smells like bitter almonds and dissolves freely in water. Water containing potassium cyanide dissolves *gold,* but has little or no effect upon the other substances usually present in gold ores.

The crushed ore, which has flowed off the copper plates, is placed in large tanks and treated with water containing one per cent. or less of potassium cyanide. By means of pumps, the liquid is made to circulate through the tanks. In 24–48 hours the gold has dissolved and the liquid is passed through boxes packed with zinc shavings, where the gold deposits as a black spongy mass, which is afterward melted. This process is very cheap and efficient. It is also largely used for sandy deposits like those referred to in (1) of the preceding section.

37. Properties of Gold.—Gold is bright yellow and nearly as soft as lead. It is almost twice as dense as the latter. One gram of gold requires only about half as much heat to warm it 1° as a gram of silver and only about one-third as much as a gram of copper. A gold coin, therefore, feels warmer to the hand than a copper or silver coin at the same temperature. In other words, gold has a low *specific heat.*

When a bit of sulphur is struck with a hammer, it flies to pieces. But a skilled workman can beat gold into a leaf only $\frac{1}{10000}$ mm. in thickness, so thin that it allows a faint green light to pass. Closely related to this is the fact that gold can be drawn into wires of marvellous thinness. A gram can be made into a wire nearly three kilometers long.

Chemically, gold is inactive. It shows little tendency to combine with other elements. This is the reason that it is found native. For the same reason it never rusts, but retains its color and luster.

Gold can be distinguished from most metals by the fact that nitric acid has no effect upon it. In applying this test to jewelry, it must be remembered that the thin gold layer on plated objects will protect the substance beneath. The surface must first be scraped off at the point to be tested. The jeweller draws the suspected object over a black stone (touch-stone), leaving a streak of the metal. He then investigates the behavior of this streak with nitric acid.

Gold is so soft that it would wear away rapidly in use, so other metals (copper and silver) are mixed with it to make it harder. American, German and French gold coins contain 90% gold and 10% copper. British gold coins contain $\frac{11}{12}$ gold and $\frac{1}{12}$ copper. In the Australian coins the copper is replaced by silver. The jeweller expresses the fineness of his gold in "carats." A carat is $\frac{1}{24}$: therefore pure gold is 24 carats fine. Thus, the British coins are 22 carat and the American 21.6 carat. 18-carat gold is often used for rings. This contains 75% of gold. The rest is copper, or copper and silver. For most other purposes, 14-carat gold is the most suitable mixture. This is hard enough to stand wear very well, but it contains enough gold to protect it against tarnish (58.33%).

38. The Standard of Value.—Gold is the standard of value of most civilized nations. For instance, the dollar is defined as a fixed weight of gold, and anyone can take gold to the mint and have it coined by paying a small fee. The coins are regularly analyzed by chemists and the utmost care is taken to keep their fineness the same.

39. **Silver: Occurrence.**—Native copper and gold always contain silver. Lead-glance usually contains enough to pay for its extraction (up to 1%). Native silver occurs in Peru, Mexico, Colorado, Arizona, Montana and elsewhere. Nuggets weighing several hundred pounds have been found.

Silver-glance (silver sulphide) occurs in the same localities. It often crystallizes in octahedra. It is just about as dense as lead-glance (specific gravity, 7.3). It is blackish lead-gray, shining and metallic-looking. The fact that it can be readily cut into chips with a knife distinguishes it from most other minerals. Heating on charcoal with the blowpipe expels the sulphur and a bead of silver remains.

Silver can be extracted from its ores by the cyanide process. The method is nearly the same as that used with gold ores. (See § 36.)

40. **Extraction of Silver from Lead.**—We have noticed that lead-glance is almost sure to contain more or less silver as an impurity. This silver goes into the crude lead which is made from it. It is extracted by melting the lead in an iron kettle and stirring up with it 0.5%–1.5% of zinc. A layer forms on the surface and is skimmed off as it freezes. This layer contains almost all the silver.

The melted lead is treated with a fresh quantity of zinc to extract the rest of the silver. It is very much better to use the zinc in two separate portions than to put in a double quantity in one operation. Let us work out an example. Suppose that the lead contains 1% of silver and that one treatment with zinc will extract $\frac{9}{10}$ of the silver which is in the lead. Then each treatment will divide the percentage of silver in the lead by 10:

After one treatment it will contain	0.1%
After two treatments it will contain	0.01%
After three treatments it will contain	0.001%

Three treatments give a practically complete extraction. A triple quantity of zinc in the first operation would do nothing of the sort. This principle is of great importance.

41. **Basis of the Method.**—Two facts form the foundation of this method: (1) when melted zinc and melted lead are stirred up, the two liquids do not merge into one, like alcohol and water, but, like oil on water, the zinc goes to the top as soon as the stirring is stopped; (2) silver dissolves much more freely in melted zinc than in melted lead, so that the zinc, when it goes to the top, takes the silver with it.

42. **Physical Properties of Silver.**—Pure silver is white and will take a high polish. It conducts heat and the electric current better than any other substance. It is not used for electric wires because it is too expensive. Copper conducts about nine-tenths as well and is vastly cheaper. The specific gravity of silver (10.5) shows that it is heavier than copper, but lighter than lead. It can be beaten into exceedingly thin foil and a gram of it can be drawn into a wire 2 kilometers long, so that it approaches gold in malleability and ductility. Silver can therefore be readily worked into the most various shapes for ornamental objects.

43. **Chemical Properties of Silver.**—When silver is heated to 960° (a clear yellow heat) it melts. Heating to a much higher temperature causes the liquid to boil, giving the *vapor* of silver. By leading this vapor into a cooler vessel to condense it, very pure silver can be obtained. Vessels of lime must be used, since most other materials would melt. *Jean Servais Stas*, the great Belgian chemist, prepared silver of extraordinary purity in this way. He informs us that the vapor is blue and that some of it escaped into the laboratory, making the air cloudy, and giving it a metallic taste.

In pure air, silver does not rust. The tarnish which appears on the silver of the household is due to compounds of sulphur in the air, which come from the burning of coal and gas, both of which contain small quantities of sulphur compounds. The tarnish is a film of silver sulphide. The same film forms on spoons that are used with eggs or mustard, both of which contain sulphur compounds. The misleading term "oxidized silver" is applied to silver which has been artificially covered with a dark layer of silver sulphide. Silver coins carried loose in the pocket are often tarnished by the sulphur compounds of the perspiration.

Silver differs from gold and platinum in being attacked and dissolved by nitric acid.

44. **Uses of Silver.**—The silver of commerce always contains copper added to harden it. Sterling silver contains 92.5% of silver and 7.5% copper. The silver coinage of Great Britain has the same composition. That of the continent of Europe and of the United States contains 90% silver and 10% copper. **Mirrors** are made by depositing a layer of silver on glass.

From 1800 to 1850 the world's production of silver was about 650 tons a year. At present the total output is nearly 6700 tons, of which the United States and Mexico together furnish about two-thirds. Canada and Australia produce most of the remainder. The chief silver-producing states are Montana, Utah, Colorado, Nevada and Idaho.

45. **Platinum.**—In alluvial deposits of sand and gravel, in the Ural Mountains, are found heavy, steel-gray, shining scales which flatten out when struck with a hammer. Their specific gravity (nearly 20) is so much above that of the other particles present that they are easily separated by washing. They consist of *platinum*, mixed with five other metals which are much like it.

Platinum somewhat resembles silver, but it has a gray luster and is much harder. Its specific gravity (21.5) is more than twice that of silver and it melts at a very much higher temperature (1775°). The air has no effect upon it at any temperature. Nitric acid does not act upon it. It can be welded at a red heat.

Platinum does not soften or melt in the flames commonly used in the laboratory and most chemicals do not affect it, for it is a very inactive metal. For these reasons it is made into crucibles, dishes, wire and foil for the use of chemists. However, there are substances which do act upon it and which must not be heated in platinum vessels. Among these are metals, like lead, copper and zinc, which would melt with the platinum and ruin the vessel.

When heated, platinum expands at just about the same rate as glass. Hence a platinum wire, sealed through a plate of glass, does not crack the glass around it when the junction is heated or cooled. The wires which pass through glass tubes to convey the electric current in lecture-table apparatus are always platinum. Two short platinum wires carry the current into and out of the bulb in the incandescent lamp. Like gold, platinum is not at all acted upon by the liquids of the mouth, and it is more tenacious than gold. These facts have led to its use by dentists. Platinum, when set free from some of its compounds, takes the form of a velvet-black powder called *platinum black*. This also has some important uses which we shall study later. The price of platinum varies greatly. It has tripled within the last twenty years and the metal is now more expensive than gold.

46. The Platinum Metals.—The five metals which occur with platinum resemble it and are classed with it under the title "platinum metals." We can only mention two of them.

Osmium is interesting because it is the densest of all substances (specific gravity, 22.5) and one of the most difficult to melt. This last fact led to its use as the filament of the osmium lamp, which was very promising for a time, but which has been displaced by the tungsten lamp.

Iridium is white and almost as dense as osmium. It is very hard and communicates its hardness to platinum when mixed with it. Gold pens are tipped with a mixture of these two metals since the tips must be hard and must resist the action of the acids usually present in ink. The same material is used to make government standards of weight and length. It is just as unalterable in the air as platinum, and being much harder, it is less affected by mechanical wear.

Related Topics

47. Base and Noble Metals.—Lead, copper, iron and zinc rust in the air rapidly, when heated. The products are dull earthy powders, not tough like the metals, and quite incapable of being beaten into foil or drawn into wire. The early chemists called these substances "calces" (singular, calx), but they are now called "oxides." About the middle of the 17th century two particularly keen minds, the French physician Jean Rey and the English chemist Mayow, grasped the fact that *the oxides always weighed more than the metals from which they were made.* They explained this by supposing that during the heating *something was added to the metal from the air.* But the suggestion attracted little attention at the time and it was not till a century and a half later that Lavoisier followed it up systematically and showed that it was in fact the correct explanation.

Gold, silver and platinum are not converted into oxides when heated. They were called the *noble* metals, because they resisted the action of fire, and the others which yielded to it, and were cheap and abundant, were called *base* metals. Mercury stands on the border-line. It does not rust in the cold, but when heated gently in air, it is slowly changed to a red oxide. At a higher temperature, the oxide again yields the metal.

48. Alloys.—Materials which are composed of two or more metals are called *alloys.* The coinage metals, sterling silver and jewellers' gold, are examples. Here are some of the more important alloys. The composition is expressed in percentages.

	COPPER	ZINC	TIN	LEAD	NICKEL
Brass	60	40			
Gun-metal	90		10		
German Silver	50	30			20
Solder			50	50	
Bronze (Coinage)	95	1	4		
Pewter			75	25	
Nickel Coins	75				25

49. Nature of Alloys.—Are alloys to be classed as solutions, as compounds or as mere mixtures? This question must be answered for each alloy separately. Silver-copper alloy (silver coinage) seems to consist merely of crystals of copper and of silver lying side by side. It is a *mixture.* Silver-gold alloys appear to be a homogeneous *solution* of the two metals. Gun metal contains a definite *chemical compound* of copper and tin.

Many familiar facts show that some alloys cannot be classed as mere mixtures. Thus, the nickel coins, which contain 75% of copper, are white. If they were mixtures, they would be nearly as red as copper; 30% of tin added to copper, makes it completely white. Silver may contain as much as 30% of gold without showing any yellow color. The specific gravity of alloys is usually greater than the figure calculated from their composition, assuming that the metals are merely mixed. The ability of an alloy to conduct the electric current is very much less than that calculated from the conducting powers of the metals when separate. Often the alloy is a poorer conductor than either metal in it. This is the reason why copper for electric wires is so carefully purified from every trace of other metals.

Definitions

Metal. An element which is more or less ductile, malleable and tenacious, and which has the peculiar luster which we associate with substances like copper, silver and gold. (See Chap. XXIX.)

Non-metal. An element which, like sulphur, has none of the properties of a metal. (See Chap. XXIX.)

Inactive. Inert; indisposed to take part in chemical changes.

Specific Heat. The quantity of heat required to warm one gram of a substance one degree.

Touch-stone. A black stone used by jewellers in testing metals.

Malleable. Capable of being beaten out, under the hammer, into thin foil.

Ductile. Capable of being drawn out into fine wire.

Tarnish. A film of rust on a metal, destroying the luster

Alluvial. A term applied to deposits made by the action of streams.

Calx. A lusterless, earthy solid, produced by heating a metal in the air.

Alloy. A material composed of two or more metals

CHAPTER IV

ANOTHER NATIVE NON-METAL: CARBON

50. Diamond: Occurrence.—In 1870 the children of a South African farmer in Griqualand, on the border of the Orange Colony, were playing with some small bright pebbles which they had picked up. The stones attracted the attention of a miner, who perceived that they were diamonds. Thus were discovered the *Kimberly Diamond Mines*, the most important of which could all be included in a circle three miles and a half in diameter. Out of this little area has come perhaps a billion dollars' worth of gems.

Each mine is a small oval about 200 meters in diameter. The surface is yellow weathered material. Below this is a soft blue-green rock (serpentine) in which the diamonds are found to the extent of about 6 carats per cubic meter (1 carat = about 0.2 gram). Occasionally it happens that a diamond flies to pieces after being taken out of the rock. This looks as though the gems had been formed under pressure and, in fact, everything indicates that they were produced at a great depth and brought to the surface by a volcanic outflow.

51. Properties of the Diamond.—The diamond crystallizes in octahedra and in other forms. The stones worn as gems are not crystals. They are "brilliants," cut in such a way as to display the "fire" to the best advantage. The luster of the diamond is due to its enormous refracting power and to the fact that the refracting power is not only very great, but also very different for different colors, so that at one angle one gets a glint of red, at another of green, and so on. Its specific gravity is 3.5. It is the hardest of minerals, that is, it scratches all others and is scratched by none. It is inactive chemically, and is not at all affected by any liquid at ordinary temperatures. There are a few solids, like washing soda for instance, which when melted with a diamond at a red heat, will destroy it.

52. Preparation of Diamonds in the Laboratory.—The diamond has been made artificially from charcoal, by the great French chemist, *Henri Moissan*. He heated a mixture of charcoal powder and iron to a very high temperature (3000°), in a furnace heated by an electric arc (Fig. 10b). The melted iron dissolved some of the charcoal. The vessel was then taken out of the furnace and plunged into water (Fig. 11). The result was to form a crust of iron on the surface, which exerted a powerful pressure on the liquid interior. The experiment imitates, in a small way, the formation of diamonds in nature, where the pressure is due to overlying rock-masses. When the iron is dissolved away by acids, it is found that some of the charcoal has been converted into little diamonds. Some of them are shown in Fig. 12. Their small size (0.5 mm. in diameter) renders them of no commercial value.

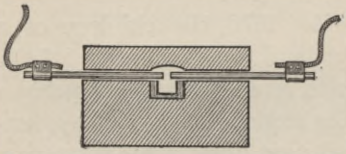

FIG. 10a.—Diagram of Moissan's furnace.

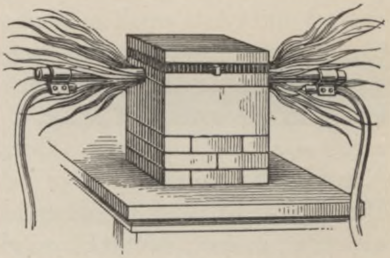

FIG. 10b.—Moissan's furnace in operation.

FIG. 11.—Cooling the crucible.

53. Uses of the Diamond.—The color of natural diamonds varies from white through yellow and brown to black. Only the pink, blue or colorless specimens are esteemed as gems: even a slight tint of yellow detracts greatly from the value. The black diamonds, most of which come from Bahia, Brazil, are largely used as an abrasive, for glass-cutting, for the cutting surfaces of rock-drills and the like.

Some very large gems have been obtained from the South African mines. The largest was the "Cullinan," found in the Premier mine on Jan. 25th, 1905, and presented to King Edward on the 66th anniversary of his birth. It weighed, before cutting, $3034\frac{5}{8}$ carats (20 oz. Troy, or more than 1 lb. 5 oz. Avoirdupois). A black diamond weighing over 3000 carats (600 grams) was found in Bahia in 1895.

FIG. 12.—Artificial diamonds.

54. **Graphite: Occurrence and Properties.**—*Graphite*, also called *plumbago* and *black lead*, is mined at Byers, Chester Co., Pa., at Ticonderoga and Hillsdale in New York, and elsewhere in the United States. Much graphite comes from Ceylon and perhaps the finest of all lead pencil graphite is brought from the mines of Eastern Siberia.

Graphite occurs in flat, six-sided crystals and in large masses which have no distinct crystalline form. It is blackish lead-gray, greasy to the touch and (like lead) it leaves a black mark on paper. Hence the name "black lead," though graphite contains no lead. Unlike the diamond, it is one of the softest of minerals, being easily scratched with the finger nail. It is less dense than the diamond, having a specific gravity of about 2. It differs also from the diamond in being a conductor of the electric current. It is very inactive chemically.

55. **Uses of Graphite.**—Like diamond and charcoal, graphite has never been melted. This causes it to be largely used when extreme resistance to heat is desirable. Crucibles

for melting metals are made of a mixture of graphite and fire-clay. The "lead" of pencils is a mixture of finely powdered graphite with fine clay carefully freed from grit. The hard pencils contain less graphite and more clay than the soft. Graphite is employed as a lubricant where oil, for some reason, will not answer, for instance in the chains of bicycles and automobiles where oil would take up dust. Stove polish is made of graphite and soap. Graphite makes excellent paint. The *electrodes* which carry the electric current into and out of electric furnaces are often made of graphite.

56. Carbon.—When graphite or diamond is intensely heated in the air, it burns away. If the air is excluded, graphite is not affected by heat, but diamond swells up and turns to graphite. Nothing is added or removed in this change; the weight of the graphite is the same as that of the diamond heated. Neither graphite nor diamond has ever been separated into simpler substances. When they are burned in the air the product is a gas which, if collected, weighs $3\frac{2}{3}$ times as much as the diamond or graphite taken, showing that something from the air has been added. Both yield the same substance. These facts show that graphite and diamond have somewhat the same relation to each other as α- and β-sulphur. They are two forms of the same element, *carbon.*[1] Anything which can be converted into graphite or diamond without loss in weight must also be a form of carbon.

57. Forms of Carbon not Found in Nature.—Using this test we can at once class as varieties of carbon three important artificial products. These are *charcoal, coke* and *lampblack.* All three change into graphite at very high temperatures without alteration in weight. All

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[1] In speaking of such forms the adjective *allotropic* is in common use. It has about the same meaning as the more familiar word "different."

three differ from graphite and diamond in being amorphous. They do not conduct the electric current nearly as well as graphite. They are not *pure* carbon. Charcoal and coke may contain 10% or more of impurities which remain, as ash, on burning the charcoal or coke in the air.

58. Charcoal.—We already know how wood behaves when heated in the air. The effect of heat in the absence of air we can learn by filling a test tube one-third with sawdust, or bits of wood, and heating slowly. Gases escape which can be lighted at the mouth of the tube, where they burn with a bright yellow flame. (Wood gas was used in one of the earliest attempts at gas-lighting in 1801, when M. Lebon lighted his estate in France with it. It has never amounted to anything practically, because better gas can be made more cheaply from coal.) Tarry liquids appear in the cooler part of the tube and charcoal remains in the bottom.

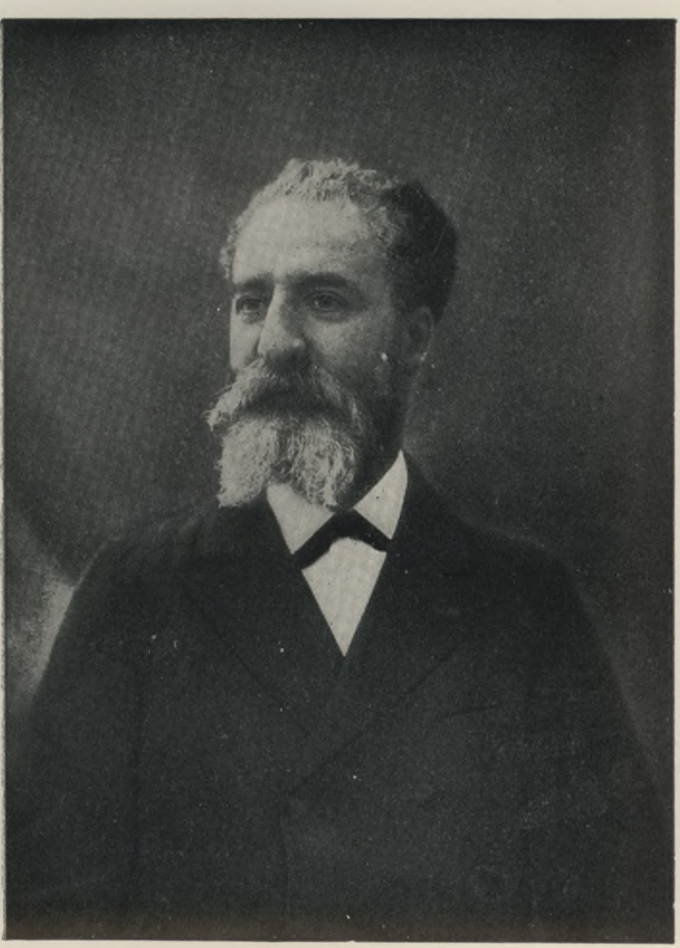
59. Manufacture of Charcoal.—In the manufacture of charcoal on a large scale, a large horizontal iron cylinder is used. The wood is heated by outside coal-firing for twelve hours. The liquid products are led away by tubes from the cylinder and collected, for they contain substances which find a ready market. Among these are *wood alcohol* (used in the manufacture of varnish and for many other purposes) and *acetic acid* (the substance which gives vinegar its sour taste. Vinegar is not made from the acetic acid of wood, but the latter has many uses in chemical industry).

60. Properties of Charcoal.—Charcoal floats on water, but this is because it is extremely porous. Its real specific gravity varies from 1.5 to 2 in different specimens. A high temperature in the preparation makes the charcoal gray-black, dense, a better conductor of the electric current and more difficult to ignite. Charcoal made at a low temperature is dead black or brownish and so inflammable that it sometimes ignites when removed from the cylinder in which it is made.

61. Conversion of Charcoal into Graphite.—Evidently the high temperature charcoal resembles graphite more than the low temperature charcoal does. Electric light carbons are made of a dense kind of carbon obtained from the gas works. The examination of a burnt-out carbon shows that the end which has been in the arc is soft, gray, metallic and greasy to the touch. The very high temperature (4000°) has changed the heated portion to graphite. The filament of an ordinary incandescent lamp is charcoal when the lamp is new. But, on opening a lamp which has burnt out it is found that the filament has been converted into graphite. Probably there will also be a film of graphite on the inside of the glass, which may have cut off a good deal of the light before the lamp gave out completely.

62. Carbon Vapor.—Two important conclusions follow. First, carbon, although it cannot be melted, can be converted into vapor. For this is the only way in which it could be transported from the filament to the glass of the incandescent lamp. Second, when the vapor is cooled, *graphite* is formed.

Moissan established the truth of both these statements by many beautiful experiments with his electric furnace (Fig. 10). Thus, a crucible and cover, made of charcoal, were completely changed into graphite in three minutes. But the crucible held its shape perfectly and the cover did not stick, as it would have done if there had been any melting. He heated charcoal in an electric furnace in which there was a copper tube, kept cold by a rapid current of water passing through it. The cold surface of the copper cooled and condensed the carbon vapor, produced by the heating of the charcoal, and graphite crystals were the only product. He never obtained the slightest evidence of melting of the charcoal or the graphite. Remembering that the change of one modification of carbon to another takes place only at the highest



HENRI MOISSAN

B. Paris, 1852. D. 1907

First prepared fluorine. Made extensive studies of the behavior of substances at high temperatures in the electric furnace, one of the results of which was the preparation of calcium carbide. Melted and vaporized lime. Prepared the diamond artificially.

temperatures (say 4000°) we can state the facts as follows:

Graphite is formed when any other modification of carbon is heated.

Graphite at the temperature of the electric arc passes directly into carbon vapor without melting.

Carbon vapor, when cooled, produces graphite, no liquid carbon being formed.

63. Coke.—*Coke* bears the same relation to soft coal (bituminous coal) that charcoal does to wood. It is made by heating soft coal, away from air, until everything which can be driven off by heat has escaped. This is done in furnaces which may be 10 meters long, 2 meters high and 0.5 meter wide, and which are heated from the outside by numerous Bunsen flames. The furnaces are made narrow, so that the heat can penetrate to the center of the mass. The flames are fed by the gas from previous charges, which is stored in gas-holders; the process yields more gas than it consumes, so that a surplus is available for other purposes. The valuable products which escape are led off through tubes and purified. Among them are illuminating gas (used about the plant), ammonia water, benzene, creosote (excellent for protecting wood against decay), carbolic acid (disinfectant), tar-camphor and pitch. Coke is gray-black and is harder and denser than charcoal. It is the great fuel of the iron industry, and is made in enormous quantities for use in the blast furnace.

When a mixture of 97% of coke with 3% of iron-filings is heated in an electric furnace, the coke is changed to graphite. Two heavy carbon rods carry a current into opposite ends of the mass. Between them the current, which is a strong one, passes through the coke and, since it is a bad conductor, a very high temperature is produced. The change of coke to graphite is due entirely to the high temperature; the current serves only as a means of supplying heat. The change is accelerated by the iron, but the latter finally vaporizes, so that the finished product is free from iron. The graphite is much purer than the coke, because the impurities, which usually remain as ash when coke is burned, are driven off in vapor by the intense heat.

64. Lampblack.—Lampblack is nothing but pure soot. We can easily make some by holding a bit of crayon in the yellow flame of the burner. On a large scale, the best grade of lampblack is made by a method the same in principle. A circle of flames burning from a horizontal perforated iron gas-pipe strikes the lower surface of a circular cast-iron vessel which rotates slowly on a vertical axis. The vessel is kept full of running water, to cool it. A scraper automatically removes the lampblack as it collects. Because of its cheapness, natural gas is used in this process. Lampblack is also made by burning substances like rosin, turpentine or petroleum in such a way that the air supply is insufficient and therefore much soot is produced. The smoke is led through chambers in which the lampblack deposits on the walls, or on cloths hung up for the purpose.

Lampblack is a velvety, jet-black powder, which shows no trace of crystallization. Its specific gravity is about 1.8 but varies in different specimens. The temperature of the electric furnace transforms it into graphite. It is used in the manufacture of printer's ink, India ink and shoe-polish. Since it is entirely unaffected by the weather, it makes excellent black paint.

65. Coal.—Pure carbon, when heated in the air, burns away completely. *Coal* cannot, therefore, be pure carbon. Pure carbon, heated in the absence of air, is unaltered at a yellow heat. Therefore the soft or bituminous coals, which, when heated, give off 15–50 per cent. by weight of various substances, leaving a residue of coke, must be very different indeed from pure carbon. However, carbon is the chief constituent of all coals, and their value as fuel depends largely upon this fact.

The two chief varieties of coal are anthracite and bituminous. Here are some of the properties of both:

PROPERTIES OF ANTHRACITE AND BITUMINOUS COAL

	ANTHRACITE	BITUMINOUS
Luster	bright, almost metallic	greasy to pitchy
Specific Gravity	1.5	1.3
Tenacity	tough	fragile
Flame	pale-blue	yellow, smoky
Effect of heat in absence of air	almost unaltered	forms coke (see above)
Percentage of free carbon	85–93	60–70
Percentage of ash	10 (varies greatly)	10 (varies)

66. Importance of Coal.—The world's output of coal each year is about a billion tons and this enormous figure is a striking proof of the relation of this form of carbon to modern life. Civilization is based upon it. Its energy warms and lights our homes, drives our machinery and transports us over land and water.

How long the coal supply will hold out is an interesting question. The estimates of geologists range from one century to ten. The amount mined is constantly increasing. Unless some substitute is found, there will be a radical change in the conditions of life when the coal is gone.

Our methods of utilizing coal are extremely crude. The waste begins at the mine, where the coal is taken out in such a way that much of it can never be mined at all. A good modern steam engine converts only about one-tenth of the total energy of the coal into useful work. In lighting by electricity less than one per cent of the energy of the coal is converted into light. The fraction which is usefully employed in ordinary cooking can hardly be greater. One third of the ashes discarded by the average household consist of unburnt coal. Such losses would not be tolerated in any other line of work.

67. Carbon Disulphide.—Having studied carbon and sulphur separately, it will be of interest to learn something about the *compound* of the two. Here again we notice an abrupt change of properties, for *carbon disulphide* is quite unlike either of its constituents. It is a colorless liquid, which passes easily into a vapor. Prolonged inhalation of the vapor is injurious. When the liquid is poured into water, a trace dissolves, but nearly all of it forms a layer below the water. From this it follows that its specific gravity is greater than that of water. When stirred up with *alcohol*, carbon disulphide forms a homogeneous liquid, no matter what proportions of the two liquids are taken.

Carbon disulphide is very inflammable. Its vapor takes fire at a temperature (120°) only a little above the boiling-point of water and great care is required in handling it.

We have seen that carbon disulphide dissolves sulphur. It also dissolves rubber and is used in the vulcanizing process. It dissolves oils and fats and is employed in extracting them from substances like olives and palm kernels. It is destructive to moths and other insects and to fungi. Parasites which attack the roots of plants can be destroyed by pouring a little carbon disulphide into a hole near the plant and then plugging the hole to prevent the liquid from evaporating. Care is necessary, for too much carbon disulphide will injure the plant.

68. Formation of Carbon Disulphide.—Carbon disulphide is obtained by the interaction of sulphur vapor and red-hot charcoal in a closed furnace, electrically heated. Graphite rods carry the current through the walls of the furnace and the space between these rods is filled with pieces of coke. The space above contains the charcoal and sulphur. When the current passes through the badly-conducting coke, a high temperature is produced (see artificial graphite, p. 43). The sulphur is vaporized and the charcoal becomes red-hot. The two combine and the carbon disulphide vapor is led away and, by cooling, converted into a liquid (condensed).

Definitions

Brilliant. A shape into which diamonds are often cut, to display the luster.

Carat. A unit of weight, used by jewellers for diamonds and other gems. One carat =0.200 gram. The diamond carat must not be confused with the carat used to express the fineness of *gold.* (Chap. III.)

Allotropic. A term applied to two forms of the same element, differing in properties.

Filament. The solid thread which serves as a source of light in the incandescent lamp.

CHAPTER V

THE ATMOSPHERE: A MIXTURE OF NON-METALLIC GASES

69. Weight of the Air.—The fact that the *air* is a real substantial thing is sufficiently shown by its destructive effects when put into rapid motion during storms. Being material, it must have weight, and this is easily proved, even with the roughest balance. Fig. 13 represents a liter flask closed by a stopper carrying a short glass tube. This tube connects with a piece of rubber tubing which can be closed by a clamp. The apparatus is weighed, the air removed by an air-pump and the clamp closed. Reweighing will show a loss amounting to about 1.2 gram. A loss only $\frac{1}{10000}$ as great could easily be detected with a fairly good balance. By a careful experiment of this kind, it can be shown that a liter of air measured at 0°, the melting-point of ice, and when the barometer stands at a height of 760 mm., weighs 1.293 grams. Since a liter of water weighs 1000 grams, the specific gravity of air is $\frac{1.293}{1000}$ or .001293 (about $\frac{1}{773}$).

FIG. 13.—Apparatus for determining the weight of a liter of air.

Roughly, we may say that water is about 800 times as dense as air; yet the total weight of the atmosphere is enormous. Stated in kilograms, it is represented by the number 52 followed by seventeen ciphers. This is usually written thus: 52×10^{17}. The expression has exactly the same meaning as the number written out in full, and it saves much space and confusion.

70. Pressure of the Air.—At the surface of the earth, the average pressure of the air is equal to 1033.6 grams (more than the weight of one kilogram) on every square centimeter of the surfaces exposed to it. This corresponds to about 14.6 pounds per square inch. It is known as the *pressure of one atmosphere*. The total weight of the air is obtained by multiplying 1033.6 g. by the area of the earth's surface in square centimeters.

71. Chemical Study of the Air.—Among the laboratory studies is one in which we heat iron, copper and tin in the air. The facts established in that exercise furnish the starting-point from which we shall attack the problem of the chemical nature of our atmosphere. Let us recall them:

(1) The metals are converted into lusterless powders, called *oxides*.

(2) Air is essential to the change, for heat alone fails to produce it.

(3) The oxide always weighs more than the metal from which it is made.

How much are we entitled to infer from these three facts?

(a) From (1) it is clear that the change from metal to oxide is *chemical*, since there has occurred in each case that abrupt change of all the properties of the metals which we have learned to regard as the sign of a chemical process.

(b) Taken together (2) and (3) give ground for the conclusion that something has been added to the metals from the air. In other words, the air contains something which combines with the metals in the same way as sulphur combined with them in the laboratory study of the formation of sulphides.

The next question is whether the air consists wholly, or only partially, of this substance, and the way to answer it is to heat a metal in a confined volume of air and see whether all of the air, or only a portion, disappears when the oxide is formed.

72. Class-room Experiments.—(a) Fig. 14 represents the apparatus for a preliminary experiment. A horseshoe magnet is hung over a glass rod in a bell jar. Bits of rubber tubing slipped over the ends of the rod, and crowded against the jar, hold the rod. A supply of iron powder clings to the poles of the magnet. The open end of the jar dips into water. The burning of the iron is started by a red-hot wire introduced through the neck of the jar. Then the stopper is replaced. The iron burns feebly for a time and then goes out, much sooner than it would in the open air. The level of the water inside the jar *rises*. The jar is transferred from the shelf to the bottom of the trough, the stopper removed and a burning splint inserted. The flame is extinguished at once.

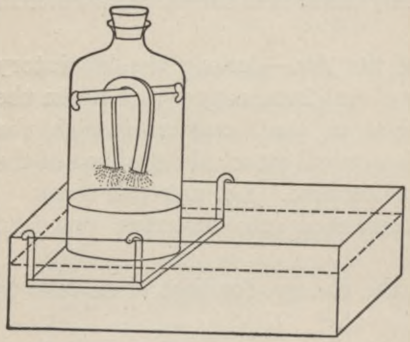


FIG. 14.—Action of heated iron on air.

(b) Place some iron powder in a porcelain crucible and wet it. Float the crucible in water and invert a small graduated cylinder over it (Fig. 15). Let stand for a week or more, noting the level of the water. There is a gradual rise, which ceases when about $\frac{1}{5}$ of the air has disappeared. The gas which remains extinguishes a flame.

(c) Quantitative knowledge can be obtained by the apparatus shown in Fig. 16. C_1 is a graduated cylinder, which is full of air when the experiment is begun. C_2 is a similar cylinder full of water. A liter of water is allowed to drop slowly into C_1; the displaced air passes over a column of red-hot copper-clippings before being collected in C_2. If the work is well done, 790 c.c. of gas will collect in C_2. Some of

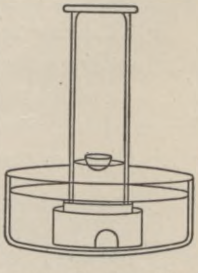


FIG. 15.—Rusting of iron in a confined volume of air.

the copper in the tube, especially in the end toward C_1, has turned black. If the gas is made to pass through the tube a second time, there is no further loss in volume. The gas collected is odorless and extinguishes flame. But if the cylinder is allowed to stand open on the desk for a few moments a flame will burn in it, showing that it is now full of air. The rapid escape of the gas upward proves that it must be lighter than air. A quantitative experiment like that indicated in Fig. 13 shows that a liter of it weighs 1.25 grams.

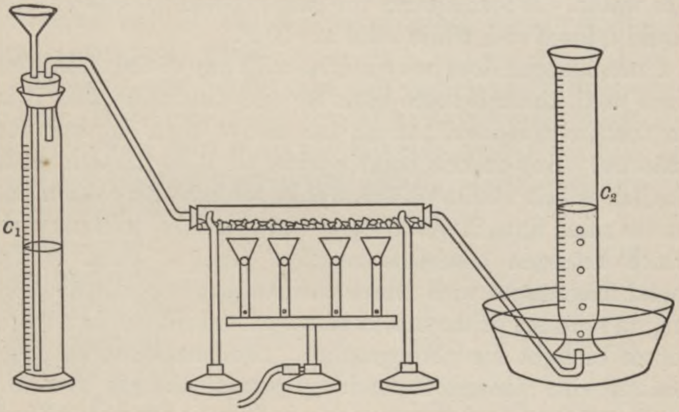


Fig. 16.—Action of red-hot copper on a measured volume of air.

73. **Nitrogen.**—Aristotle and, following him, the whole ancient and mediæval world, considered the air as a simple substance. Our experiments show that this opinion was not correct and that it contains at least two things, one of which acts on metals while the other does not. The one which does not is called *nitrogen.* It is an *element.* We have obtained it in the experiments of the preceding section, especially (c). This nitrogen is not pure, but the impurities in it are small in amount and we shall not fall into any error by using it as a basis for our study of the element. We can prepare it in the laboratory in purer condition, not from the air, but by setting it free from one of its compounds.

74. Properties of Nitrogen.—Most of the important facts about nitrogen may be learned from the laboratory or classroom experiments. It is a colorless, odorless gas, lighter than air. Since it can be collected over water, its solubility in that liquid must be slight. Like all gases, it has been condensed to a liquid by intense cold and pressure, and the liquid has been frozen to a solid. Liquid nitrogen looks like water. It forms when the gas is cooled to –194°. The liquid freezes to a white solid at –214°.

Since nitrogen does not combine with any of the metals we have used, there is some basis for the conclusion that it is an *inactive* non-metal; much less active than sulphur, for instance. But on this point a wider study of the element is needed, which would, on the whole, confirm this conclusion. At the same time, it would show that there *are* elements with which nitrogen combines readily. One of these is the metal magnesium with which the student is perhaps familiar, on account of the extensive use of its brilliant flame as a source of light for photography. The compound of magnesium with nitrogen is made by passing the gas over the hot metal, in apparatus similar in principle to that described in § 72 (c). Mercury is used instead of water. The compound is a yellow powder, called *magnesium nitride,* for the same reason that the compound of copper and sulphur is called copper sulphide. Impure magnesium nitride can be formed by simply heating a mass of powdered magnesium in the air on an asbestos plate.

Nitrogen is not at all poisonous, but it will not support life. A mouse, placed in it, dies by suffocation.

75. The Second Chief Constituent of the Air.—So far, our experiments prove that the air consists chiefly of two elements, nitrogen, and another element. To the second element, Lavoisier, in 1775, gave the name which it still bears, **oxygen.** Oxygen unites with the metals and the compounds formed are the **oxides.** Since a burning bit of wood is extinguished in air which has acted upon heated copper or iron, it would seem that oxygen is also responsible for ordinary burning.

The next task is to determine the properties of oxygen, and to do this it is necessary to prepare it in pure condition. As a raw material the oxides suggest themselves at once, for they are the only substances we have yet met (the air excepted) which certainly contain oxygen. Our problem, then, takes the form of separating an oxide into its two elements, (1) the metal and (2) the element of which we are in search. How is this to be done?

We have seen (p. 13) that *heat* drives off sulphur from pyrite. This, together with what we have learned about the action of heat upon wood and soft coal, gives some basis for the idea that high temperature is likely to have a separating or *decomposing* action upon compounds. Heating the oxides might afford the solution of the problem.

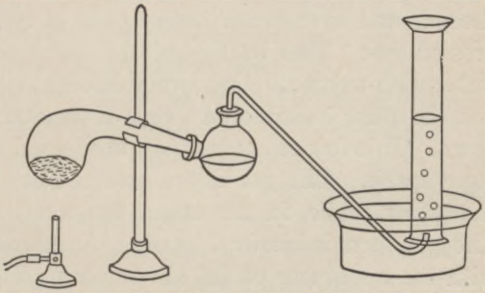


FIG. 17.—Heating the oxide of mercury.

76. The Oxide of Mercury.—Now the oxides of iron and copper *can* be decomposed by heat, but the temperature required is so high that the experiment cannot be performed with inexpensive apparatus.

When *mercury* is heated in the air, it slowly passes into a dense red powder, which has been known since the middle of the 14th century, and is used in medicine and as an insecticide. This is the *oxide of mercury*. Since it can be purchased in pure condition, it is not necessary to make it.

Some mercury oxide is heated in the apparatus shown in Fig. 17. The vessel is called a *retort*. It should be made of hard glass, so as not to soften when heated. It is connected with a bulb to receive the mercury which we anticipate as one product, and the apparatus is so arranged that any gas set free will be collected in an inverted bottle filled with water.

The red powder completely disappears, if the heating is continued long enough. A metallic liquid, which we recognize as mercury, appears in the bulb. A colorless gas bubbles up through the water and collects in the bottle. This can only be the other constituent of the oxide. A splint bearing a spark bursts into flame when plunged into the gas and burns much more vigorously than in air. *This gas is the element oxygen.*

77. Properties of Oxygen.—Mercury oxide is rather expensive and, for further investigation of oxygen, it will be cheaper and save much time to use a cylinder of the compressed gas. Two bottles of the same size are filled over water with oxygen. One is placed right side up on the table and the other is placed on a ring of the stand with the mouth down. In a few moments both are tested with a splint bearing a spark. The gas in the inverted bottle does not affect the spark, while, in the other, the wood bursts into flame. The gas, then, is *heavier* than air. A quantitative experiment with the apparatus of §69 shows that a liter of oxygen at 0° and under a pressure of 760 mm. weighs 1.43 grams. We perceive that the gas is colorless and, from the fact that it is collected over water without noticeable loss, we reason that its solubility in that liquid must be small. At –183° oxygen condenses to a light blue liquid slightly denser than water, and, on further cooling, the liquid freezes to a pale blue solid. Liquid oxygen is strongly attracted by the magnet. This is a surprising fact, for magnetism is distinctly a property of certain *metals*, like iron and nickel, and oxygen is one of the most non-metallic of the elements.

78. Chemical Properties.—A simple method of ascertaining the behavior of oxygen with various substances is shown in Fig. 18. The substance is placed in the bowl of the iron spoon, heated until it begins to burn, and then plunged into a bottle of the gas. In this way it can be shown that zinc and iron burn in oxygen and that the products are the same as those obtained by burning the same metals in the air, that is to say, zinc oxide and iron oxide. The experiment can be varied by making a heap of the powdered metal on an asbestos plate, letting a burner flame play upon the heap till it glows and then directing a stream of oxygen from the cylinder upon the metal by means of a glass tube. Iron, zinc and some other metals burn vigorously to their oxides when treated in this way. Energetic burning of this kind, accompanied by the escape of light and much heat, is called *combustion*.

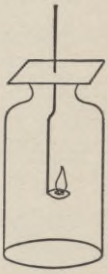


FIG. 18. — Combustion in oxygen.

Sulphur, heated in a spoon, burns languidly in the air, but in oxygen the combustion becomes energetic. The product is a colorless gas with a sharp suffocating odor, which must, of course, be an oxide of sulphur.

If we went through the list of the elements, trying the behavior of all of them with oxygen, we should find a few, like gold, platinum and some others, upon which the gas has no action. But most of them would unite with it, either rapidly, like those just mentioned, or slowly. Oxygen, then, is a very *active* element.

Free oxygen is essential to the life of animals. In its absence, death by suffocation results, even when the gas in which the animal is placed is non-poisonous. It is also essential to the life of the ordinary plants. Some simple plants (fungi and micro-organisms) are able to live without it.

79. The Air a Mixture.—We are now ready to take up the important question whether the nitrogen and oxygen of the air are *chemically combined* or merely *mixed;* whether the air is a *mixture* or a *chemical compound* of the two gases. This question can be answered with practical certainty by comparing the properties of oxygen and nitrogen, on the one hand, with those of air on the other. The properties of air are those of oxygen modified by those of nitrogen. Thus the air supports the combustion of substances in the same way as oxygen does, but less energetically, because the nitrogen interferes. Compare the burning of sulphur in air with its burning in pure oxygen. Since air contains only about $\frac{1}{5}$ of its volume of oxygen, there is about five times as much oxygen in 1 c.c. of pure oxygen as in 1 c.c. of air. So the sulphur burning in pure oxygen is supplied, on the whole, five times as freely with the oxygen to burn it, and, naturally, it burns more rapidly. On high mountains substances burn much more languidly than they do at ordinary levels, because the air is rarefied and the weight of oxygen in 1 c.c. is less.

When a liter of oxygen is mixed with 4 liters of nitrogen from § 72 (c), the mixture is air in all essential respects. No heat or light escapes during the mixing. There is no abrupt change of properties: the properties of the mixture are simply those of the two gases. In fact the properties of air can be *calculated* from those of its two chief elements. In order to understand this, let us calculate the weight of a liter of air. 1 liter of the nitrogen from § 72 (c) weighs 1.257 grams.

In 100 liters of air there are 79 liters of nitrogen. The weight of this nitrogen will be:

$$1.257 \times 79 = 99.3 \text{ grams}$$

The weight of the oxygen will be:

$$1.43 \times 21 = 30 \text{ grams}$$

The total weight of the 100 liters of air will be:

$$99.3 + 30 = 129.3 \text{ grams}$$

And the weight of 1 liter will be:

$$129.3 \div 100 = 1.293 \text{ grams,}$$

which agrees with the result obtained by directly weighing the air in § 69, p. 48.

In this way, other properties of air can be calculated. But a chemical compound is a *new* substance with its own properties, and they can only be determined by experiment.

Our results indicate strongly, therefore, that the nitrogen and oxygen in the air are not chemically combined. But if air is a mixture the percentage of oxygen in it must vary, since only compounds have an invariable composition. If we were to carry out the experiment of § 72 (c) many times with different samples of air from various places and elevations, would the loss of volume in passing over the hot copper always be the same?

The answer is that the method is not accurate enough to answer the question we have put. The error, even when the experiment is carefully worked, may be as great as 1%. There are much more exact ways of analyzing the air, and these methods have shown that the percentage of oxygen does, in fact, vary from 20.86 to 20.99. This variation is an absolute and final proof that the air is a mixture. No further evidence is needed. However, in the next chapter we shall see that when air dissolves in water it dissolves as a mixture. Further on in our work it will be shown that, when air is liquefied, the behavior of the liquid shows clearly that it is not a compound.

Related Topics

80. History of Oxygen and the Atmosphere:—Carl Wilhelm Scheele.—Oxygen was discovered about 1771 by the Swedish chemist *Scheele,* who obtained it by heating mercury oxide and by other methods. His apparatus is indicated in Fig. 19, which is a reproduction of his own drawing. The retort containing the mercury oxide was heated by a charcoal fire, for the manufacture of gas dates only from 1812.

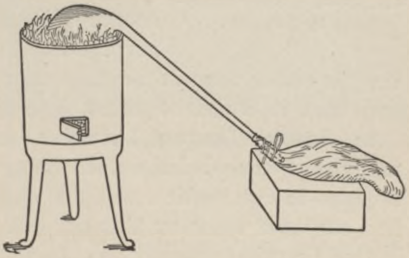


FIG. 19.—Discovery of oxygen by Scheele.

When the bladder was distended with oxygen, it was closed by a string and another bladder tied on in its place. He called the gas "fire air" on account of the violent way in which substances like charcoal and sulphur burned in it. He knew that the gas was essential to the life of animals, and he often called it "vital air," for this reason.

Scheele knew that the atmosphere was not all "fire air." By allowing iron filings to rust in a confined volume of air over water he removed the oxygen and obtained *nitrogen.* This he called "vitiated air" because it did not support combustion or respiration.

These and many other great discoveries were contained in Scheele's book, "A Treatise on Air and Fire," which is one of the classics of our science. His publisher refused to print the book until 1777, and, in the meantime, both nitrogen and oxgyen were independently discovered by British chemists.

81. Rutherford and Priestley.—In 1772 *Daniel Rutherford,* a young Scotch physician, obtained nitrogen in somewhat the same way as Scheele had done.

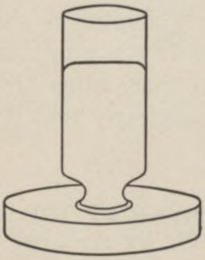
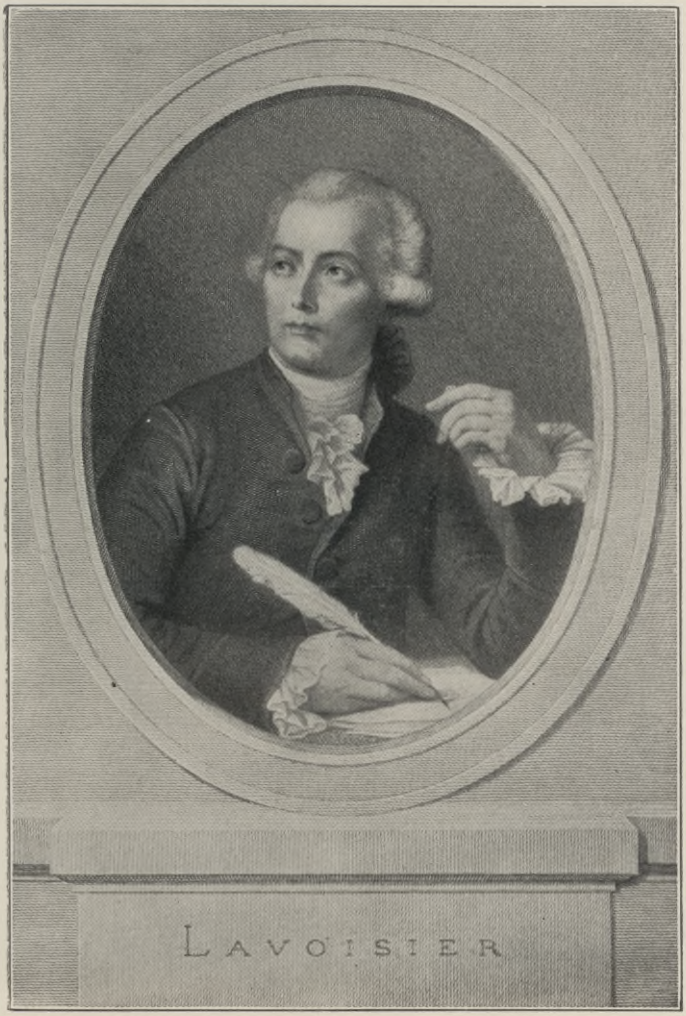


FIG. 20.—Discovery of oxygen by Priestley.

On Aug. 1, 1774, *Dr. Joseph Priestley,* an English clergyman, without knowing anything of Scheele's work, obtained oxygen by heating mercury oxide. The red powder was contained in an inverted tube containing mercury, and dipping into more mercury in a dish. The rays of the sun, focussed by a lens, formed the source of heat (Fig. 20). Priestley was surprised to find that a candle burned in the gas better than in air, that mice inhaled it without injury, and that it could be taken into his own lungs without pain.

82. Antoine Laurent Lavoisier.—Although Scheele had prepared oxygen and determined its properties, yet the part that it plays in combustion was not clear to him. Priestley, also, had confused ideas on this subject. We have seen that light in this direction can only be obtained by *quantitative* work. This work was done by Lavoisier, who was born in 1743 and was



One of the first to make exact quantitative experiments. Explained the function of oxygen in combustion and respiration. Showed that the diamond burns to carbon dioxide. First clearly stated the law of the indestructibility of matter. Reformed the language of chemistry and wrote the first systematic text-book on the subject.

guillotined in Paris, on baseless and absurd charges, during the Reign of Terror, on May 8, 1794.

Taking his stand upon exact quantitative experiments, Lavoisier explained the behavior of oxygen in combustion, in the conversion of metals into oxides, and in respiration, and his views have guided the progress of our science ever since. Perhaps the most important part of his work was to place the *balance* in the position which it still holds, as the chief tool of the working chemist.

83. Lord Rayleigh and Sir William Ramsay.—In 1894 Rayleigh undertook to ascertain with the utmost exactness the weight of a liter of nitrogen. He met with the surprising difficulty that the weight of a liter of the gas depended upon the way in which it was made. When the nitrogen was set free from a nitrogen compound the weight of a liter of it was 1.2505 gram. The results obtained with the gas from five different nitrogen compounds agreed closely. But nitrogen obtained from the air, by the method of § 72 (c), was always heavier: a liter of *atmospheric* nitrogen weighed 1.2572 gram. This difference was far greater than the possible error in Rayleigh's work and, to explain it, he suggested that atmospheric nitrogen was not pure, but contained a small quantity of some denser gas which had not yet been separated.

84. Argon.—We have seen (p. 52) that nitrogen combines with hot magnesium. Rayleigh and Ramsay passed atmospheric nitrogen many times through a hot tube containing magnesium powder. About 1 % by volume remained unabsorbed, and this was the new gas of which they were in search. It is colorless, odorless, more soluble in water than is nitrogen and more easily liquefied. They named it *argon*, which is from the Greek and means inert.

85. The Inactive Elements.—The name argon refers to an extraordinary property of the gas. Since the air contains nearly 1 % of argon and since it had never manifested its presence in any way, it was clear that it must be a very inactive element. Careful work led to the surprising fact that it was *totally* inactive. Rayleigh and Ramsay were unable to get it to enter into any chemical change, and all subsequent attempts have failed, like theirs. *Compounds of argon are unknown.*

Further work by Ramsay has shown that, in addition to argon, the air contains slight traces of four other colorless gases which, like it, are totally inactive chemically. These gases are *Helium*, *Krypton*, *Neon* and *Xenon*.

Definitions

Centimeter. One-hundredth of a meter.

Millimeter. One-thousandth of a meter; one tenth of a centimeter.

Square Centimeter. The area of a square whose side is one centimeter.

Cubic Centimeter. The volume of a cube whose side is one centimeter.

Liter. The volume of a cube whose side is ten centimeters; one thousand cubic centimeters.

Gram. The weight of a cubic centimeter of water at the temperature at which water is densest (4°). Roughly, this is one-fifth the weight of a nickel five-cent piece.

Kilogram. One thousand grams; about 2.2 pounds.

Nitride. A compound of nitrogen with another element.

Decompose. To separate a compound into its elements, or into simpler compounds.

Combustion. Rapid chemical combination attended by the production of light and heat.

Quantitative. A term applied to experiments in which the *quantities* of the substances used, and of the products, are determined by accurately weighing them.

CHAPTER VI

THE GENERAL PROPERTIES OF GASES.—THE LAWS OF BOYLE AND CHARLES.—THE KINETIC THEORY OF MATTER[1]

86. Solid and Liquid.—Iron is always called a *solid,* water a *liquid* and air a *gas.* Let us consider just what is meant by this. The most striking distinction is that a piece of iron has a shape of its own, which it retains; the air and the water have not. Their shape depends upon that of the vessel which happens to contain them. To change the shape of the iron, work is required: the iron opposes a resistance to the change which, within limits, is proportional to the change in shape enforced upon it.

But is the idea that a liquid has no shape quite exact? Think of a raindrop. It is not in any containing vessel, and the fact that it is falling freely removes it from the influence of the earth's attraction, so far as change of shape is concerned. Raindrops are *spherical.* By mixing the right quantities of water and alcohol, one can prepare a liquid which has the same specific gravity as olive oil (0.92). If drops of olive oil are placed in this liquid, they float about freely at any level, and always take the form of spheres.

We may say, then, that a solid has its own shape, which work is required to change; that very little work is required to alter the shape of a liquid, which is usually that of the containing vessel; and that the shape of a liquid freed entirely from any external action, is that of a sphere.

87. Gases.—Let us try, now, to establish some distinctions between the water and the air. We know already that air is vastly lighter than water. This is a general distinction

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[1] The full treatment of these subjects belongs to Physics. The present chapter aims only to give an elementary account of those topics which are of special importance in the chemical work.

between liquids and gases. Since the specific gravities of different liquids are very different and since gases also vary greatly among themselves in this respect, no definite numerical statement can be made about the matter. If an average was made of the specific gravities of all liquids and the same was done with the gases the relation of one to the other would probably be of the order of 1000 : 1.

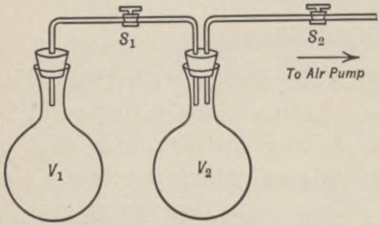

FIG. 21.—The expansion of a gas into a vacuum.

If we pour half a liter of water into a liter bottle, the water remains in the bottom, and its upper surface is distinct. All liquids behave in this way but gases never do. Half a liter of gas admitted into an empty liter bottle, from which all gas has been removed by an air pump, will fill the bottle completely.

In the diagram (Fig. 21) the vessels V_1 and V_2 have each a capacity of 1 liter. They are connected by a tube with a stopcock S_1. From V_2 another tube with a stopcock S_2 leads to an air pump. Close S_1, open S_2 and exhaust V_2. Then close S_2 and open S_1. The liter of air in V_1 at once distributes itself evenly between the two vessels, and the air pressure in the apparatus becomes one-half of its value at the start. If the process is repeated, the same thing occurs again, and the pressure is reduced to one-fourth its original value. Two important distinctions between liquids and gases are, then, (1) that the density is much higher in the liquids, the material is more closely packed in them; (2) that they form an upper surface in a vessel which they only partly fill, while the gases expand and fill the vessel completely.

FIG. 22. — The diffusion of gases.

88. Diffusion of Gases.—In Fig. 22 C_1 and C_2 are two cylinders of the same size ground to fit air-tight. The upper cylinder C_1 is filled with nitrogen and the lower with oxygen. Nitrogen is decidedly lighter than oxygen; yet the two gases mix, and in a little while we find in all parts of both cylinders a mixture containing 50% of each gas by volume. Other pairs of gases act in the same way. Each gas travels into the other until there is a uniform mixture. This is called the *diffusion of gases.* It means that actual *motion* of both gases from one part of the apparatus to another has occurred. It takes place even when the cylinders are left entirely at rest, and when change of temperature is excluded.

89. Diffusion in Solids and Liquids.—This behavior is not peculiar to gases. We may use alcohol and water in the two cylinders, putting the alcohol in the upper one, because it is lighter. The result will be a uniform mixture of the two, but a longer time will be required than in the case of the two gases.

When a cylinder of lead is placed with its lower surface on a disk of gold, gold travels upward into the lead, slowly in the cold and more rapidly when heated. In the same way gold will travel into silver and platinum. When the silver is stripped from an old piece of silver plate it is found that silver has penetrated into the base metal, and can be detected some distance below the surface.

90. Effect of Pressure upon Solids, Liquids and Gases.—A cube of iron 10 cm. on the edge has a volume of 1 liter. Under ordinary circumstances the pressure on it is that of the atmosphere, which does not depart widely from 760 mm. of mercury. This means that each square centimeter of the block is pressed as though it supported the weight of a column of mercury 1 sq. cm. in cross section and 760 mm. high. Now imagine the cube placed in a suitable apparatus and subjected to double this pressure. It would, of course, be squeezed into a smaller bulk, but the shrinkage would be very small, so small that it would be difficult to detect. If we attempted to compress the block till its volume was reduced to half a liter, we should find that the pressure required was beyond the power of any apparatus and that breakage would put an end to the experiment long before the result was achieved.

A similar experiment with a liter of water would give about the same result. Doubling the pressure to two atmospheres would scarcely reduce the volume and we should find that to halve the volume would require the application of pressures which cannot be handled with our present appliances. Other solids and liquids would behave in about the same way as iron and water. Not in *exactly* the same way, for the reduction in bulk caused by doubling the pressure would be different for each substance, but it would be slight in all cases and halving the volume by pressure would be quite out of the question.

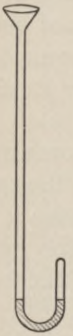

FIG. 23.—Boyle's Law.

A liter of air under pressure behaves in a very different and much more simple way. Raising the pressure to two atmospheres reduces the volume to 500 c.c. If the pressure was doubled again, the volume would become 250 c.c. If the pressure was doubled a third time to 8 atmospheres the space occupied by the air would shrink to 125 c.c. and so on.

The apparatus shown in Fig. 23 affords a simple method of verifying this law. The air is contained in the short closed limb of the tube and mercury is poured into the open limb until the two columns of mercury are of the same height. The volume of air is then recorded. The pressure is that of the atmosphere, say 760 mm. If, now, sufficient mercury is poured into the open limb to cause a difference of level of 760 mm. between the surfaces of the columns of mercury in the two limbs, it will be found that the volume of the air is exactly halved. Other gases behave in the same way.

We may now sum up the results in a general statement: *At a fixed temperature, the volume of any mass of gas varies inversely as the pressure upon it.* This is called **Boyle's Law,** after the great Irish chemist Robert Boyle, who first stated it in 1660. Or, we can say that the closeness with which the matter of the gas is packed is proportional to the pressure; twice the pressure forces twice the material into 1 c.c. The closeness of packing, the quantity of a substance in 1 c.c., is called the *concentration.* So that we can put the same law into another form: *The concentration of a gas is proportional to the pressure.*

Notice how much simpler the conduct of the gases is than that of the solids and the liquids. Each solid and each liquid behaves in its own way, and there is no simple relation between pressure and volume. But all gases behave alike, and the relation between volume and pressure is of the simplest sort. The method of using Boyle's law in calculation is explained in detail in Chap. XXX.

91. Effect of Temperature upon the Volume of a Mass of Gas.—Returning to our block of iron, let us suppose that its volume is exactly 1 liter at 0°. If it is warmed to any higher temperature, it will expand, and its volume will become greater. This expansion is different at different temperatures, but, on the average, about three hundred-thousandths of a liter (0.00003 liter) would be added to the volume of the block for every degree centigrade it was heated. Other solids would behave in about the same way, but the expansion, though of the same order, would be different in amount for each. A cube of copper would expand somewhat more per degree than the iron; a cube of platinum very much less.

Our liter of water, measured at 0°, would *contract* when heated until 4° was reached, after which it would expand in a very irregular way. The expansion becomes greater at high temperatures. On the average the amount added to the volume for each degree rise in temperature would be about

0.0004 liter. We can say, roughly, that the water expands rather more than ten times as much as the iron.

Each liquid behaves in its own way. Alcohol expands more per degree than water, mercury only about half as much, and more regularly.

If we should measure a liter of air at 0°, and warm it, we should notice that it expands about ten times as much as the water and about a hundred times as much as the iron, adding 0.00366 liter—that is $\frac{1}{273}$ liter—for every degree through which it is warmed. We should note also that the expansion is wonderfully regular. A rise of 1° in the neighborhood of 100° increases the volume to exactly the same extent as the same rise in temperature in the neighborhood of 0°. Finally, if we tried different gases, nitrogen, argon, oxygen and so on, we should get the surprising result that the amount of expansion of each is almost the same. *A gas expands* $\frac{1}{273}$ *of its volume at 0° for every degree through which it is heated.* This statement is called **Charles' Law.**

The law will become clearer, if, instead of starting with a liter, we think of 273 liters of gas at 0°. Then we should have

at 1°	274 liters
at 2°	275 liters
at 3°	276 liters
at 20°	293 liters
at 100°	373 liters
at 273°	546 liters

The law is the same when the gas is cooled. 273 c.c. of gas at 0° become:

at –1°	272 liters
at –2°	271 liters
at –3°	270 liters
at –20°	253 liters
at –100°	173 liters

at –273°, the **absolute zero** of Physics, if the gas continued to contract regularly, the volume would become zero and the gas would disappear. This, of course, is absurd, and it means simply that we have applied the law at temperatures at which it no longer holds good. Temperatures around –272° have actually been obtained. At such temperatures all gases except helium become solid, and the law of contraction loses its meaning.

So far, then, as the effect of heat goes, gases differ from solids and liquids in three important respects:

1. They expand very much more for equal increase in temperature.

2. The expansion is almost perfectly regular.

3. The expansion is almost the same for all gases.

The method of applying Charles' Law in practical calculation is explained in Chap. XXX.

92. The Kinetic Theory.—The behavior of gases with respect to temperature, their behavior under pressure and their diffusion (§88) make up a remarkable group of properties. In 1738 Daniel Bernoulli constructed an hypothesis which explains these properties so perfectly and which is so strongly supported by very recent research that it has ceased to be an hypothesis and has become a fact. Since there is hardly any doubt that it gives a picture of the actual structure of gases —and, to some extent of solids and liquids—and since it has important applications to chemical work, it must be thoroughly understood.

A liter of oxygen, measured under ordinary pressure, can be squeezed by increased pressure into a volume of about 1 c.c. There are two ways, and only two, of looking at this fact: (1) The actual *matter* of the gas is compressed until it occupies only about $\frac{1}{1000}$ of the original space; (2) the gas did not really fill the volume of 1 liter in the first place, because it is composed of particles with large spaces between them; under pressure, the particles are pushed more closely together, the matter becomes more densely packed.

The kinetic theory of Bernoulli starts from the second idea. A gas is composed of particles which are separated by spaces very large in proportion to the size of the particles. How, then, are we to explain the fact that a mass of gas completely fills any vessel in which it is placed? At first thought, we should expect a liter of oxygen to settle until the particles were in contact, forming a thin layer upon the bottom of the vessel and leaving the space above empty.

There is an easy answer to this question. The particles are not at rest, but in rapid, continual motion in straight lines. Each moves until it strikes another, or the wall of the vessel, when it rebounds in some new direction. Imagine a lot of billiard balls, rolling about and continually rebounding from each other and the rim of the table. Imagine also that the balls are perfectly elastic, so that no motion is lost during a rebound, and the movement will keep up forever. Finally imagine that the motion takes place in three dimensions instead of in two. Or, think of a swarm of angry, tireless bees, shut up in a box.

93. **The Molecules.**—We shall call these particles **molecules.** The average speed of a molecule of oxygen is about that of a rifle bullet, say half a kilometer per second. In our illustration of the billiard balls, it is plain that there would be continual violent blows against the rim of the table. Now if the balls were very numerous, these blows would be delivered so frequently that they would no longer be perceived separately. Instead of a series of shocks they would produce the effect of a steady pressure. *The pressure of a gas is the bombardment of the molecules against the surface pressed.*

If a liter of oxygen is squeezed into half a liter there must be twice as many molecules in each cubic centimeter of the gas as before. Hence twice as many molecular blows will be delivered per second against every square centimeter of the surface in contact with the gas—the pressure will be doubled. For the same reason, if the gas is squeezed into one-fourth of a liter, the pressure will be four times as great as at the start, and so on. This is *Boyle's Law.*

94. **Diffusion.**—Diffusion (§88) is a direct result of the movement of the molecules. The forward movement of the

molecules of oxygen carries them up into the nitrogen, while the molecules of nitrogen move downward. Other pairs of gases act similarly. Returning to our billiard-ball illustration, if we imagine that, at the start, the balls on one-half of the table were all red and those on the other half all white, it is plain that in a little while they would be uniformly mixed. Or, using the other simile, if we imagine that, at the beginning of the experiment, the upper half of the box was occupied by wasps and the lower half by bees, we see at once, that after a short time, the aimless flying of the insects would mix them uniformly.

The diffusion of alcohol in water (§89) proves that the molecules of liquids must also be in motion. The chief difference is that, in the liquid, the molecules are much more closely packed than in the gas, and the average distance a molecule moves before colliding with another is much shorter. The diffusion of metals into each other (§89) shows that the molecules of *solids* are in motion. But, on account of the great cohesion of solids, a molecule does not easily leave its place and move forward to a new position.

95. Visible Proof of the Motion of Molecules.—We have looked into this matter far enough to see that the theory of molecules in motion explains the behavior of gases in a very simple and satisfactory way. To proceed further requires the aid of the higher mathematics. The subject has been investigated fully by Maxwell, Boltzmann and others, who have shown that the agreement between the theory and the facts is nearly perfect. But even this does not show that the theory is *true*, for some other idea might be imagined which would explain the facts equally well.

Suppose, for illustration, that we were watching the motion of the hands of a clock. To account for this motion we might construct an hypothesis that the hands were moved by a spring which had been wound up. This would explain the motion perfectly, and yet it might turn out, after all, that the clock was run by a weight.

In order to be sure we want to *see* the motion of the molecules. This looks hopeless on account of their inconceivable smallness. Calculations based on the very theory we are now studying show that in a liter of air—or any other gas—under 760 mm. pressure and at 0°, the number of molecules is 3×10^{22}, that is, 3 followed by 22 ciphers. In order to get some idea of the magnitude of this number, suppose that we have a liter of air confined in a bottle, with a hole from which a million molecules escape every second, while nothing enters. Nearly a thousand million years would elapse before all the molecules had left the bottle.

However, we have seen that it is difficult to set limits to the progress of our science, and the task of making the molecular motion visible has recently been accomplished. In order to understand how this was done, let us start by thinking of a mote, floating in a sunbeam in still air. According to our theory the mote is being battered on all sides every second by countless millions of molecules moving with about the speed of rifle bullets. It remains at rest because it is very large and heavy in proportion to the molecules and the blows in opposite directions neutralize each other. Now imagine the mote to grow smaller until it is not very much larger or heavier than the molecules themselves. The number of molecules striking it each second will decrease, and the motion given it by the blows will increase. There must come a time when a molecule striking it, say on the right, will give it a perceptible push toward the left before another molecule will collide with it and send it back.

Recently chemists have succeeded in obtaining, floating in air, a dust of silver so fine that each grain can contain only a few molecules. When viewed under a powerful beam of electric light, with a good microscope the silver particles are seen to be darting about in a zig-zag path composed of straight lines. The motion is exactly that which our theory supposes, and it goes on without interruption or slacking up for an unlimited time. Very small particles of gold (and other metals) suspended in water, have the same ceaseless zig-zag motion, due to the collision of the moving water molecules with the particles of gold.

96. Solutions of Gases in Water.—Fig. 24 represents a glass tube which has been filled with pure, cold boiled water and inverted in a dish containing the same liquid. The object of the boiling is to drive out the gases which water always takes up from the air. A little *nitrogen* is passed up into the tube.

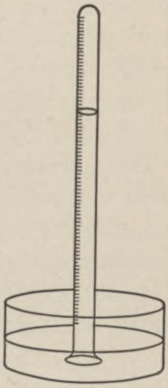

FIG. 24.—Solubility of gases.

What does the kinetic theory predict? The surface of the water will be battered by a hailstorm of nitrogen molecules. Some of them will penetrate the surface and move about among the water molecules. That is, some of the gas will dissolve in the water. But, as the number of nitrogen molecules in the liquid grows larger, more and more of them will break through the surface of the liquid upward and return to the portion of the tube occupied by the gas. When the number passing upward through the surface per second is equal to the number passing downward, no more nitrogen will dissolve. The water will be **saturated** with it. There is no reason to think that a sudden stagnation, a stoppage of everything, has occurred. The molecular storm continues, but its effects in the two directions balance. **Equilibrium** between them has been reached. Using our equation method we may write this equilibrium thus:

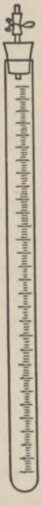

FIG. 25.—Solubility of nitrogen (quantitative).

$$\text{Nitrogen (gas)} \rightleftarrows \text{Nitrogen (dissolved)}.$$

This means simply that, in each second, just as much nitrogen dissolves in the water as is liberated from it.

Quantitative information about the solubility of nitrogen can be obtained by the apparatus shown in Fig. 25, which is a graduated tube closed by a stopper. Through the hole in the stopper passes a glass tube ending in a rubber tube bearing a clamp. The graduated tube is filled with pure water, free from air. It is clamped with the open end dipping into boiled water and a little nitrogen passed in through a rubber tube which reaches to the top. The volume of the nitrogen is read and that of the water remaining in the tube is obtained by subtraction.

The next step is to insert the stopper, close the clamp and shake vigorously. Then the clamp is opened under water and, of course, the volume of water which enters is a measure of the amount of nitrogen which has been dissolved.

In this way it is found that water dissolves very little nitrogen, and less at high temperatures than at low.

100 c.c. water dissolves at	0°	(freezing-point)	2 c.c.
100 c.c. water dissolves at	20°	(room temperature)	1.5 c.c.
100 c.c. water dissolves at	80°		0.5 c.c.
100 c.c. water dissolves at	100°	(boiling-point)	a volume too small to determine

All other gases are more soluble in water than nitrogen. Oxygen is very slightly soluble, yet it dissolves about twice as freely as nitrogen.

100 c.c. water dissolves at	0°	4 c.c. oxygen
100 c.c. water dissolves at	20°	3 c.c. oxygen

97. Effect of Pressure on the Solubility of Gases.—So far, we have supposed the nitrogen to exist at the pressure of one atmosphere. What would be the effect of doubling the pressure? The kinetic theory returns a straightforward answer to this question. Doubling the pressure will crowd twice as many molecules of nitrogen into each cubic centimeter of the gas and twice as many will strike the surface of the liquid per second. Since the amount of nitrogen taken up by the water depends upon the frequency of the molecular blows, twice as much gas should dissolve. Experiment con-

ROBERT WILHELM BUNSEN

B. Germany, 1811. D. 1899.

Discovered cæsium and rubidium. First prepared manganese and strontium in pure condition. First obtained aluminium by the use of electricity. Investigated the explosion of gunpowder and the solubility of gases in water. Invented the Bunsen burner, the Bunsen battery, the photometer, the spectroscope, the water air-pump and the ice calorimeter.

firms this prediction. A double pressure forces a double quantity of gas into the water. In general terms, *the solubility of a gas is proportional to the pressure of the gas upon the surface of the liquid.* This is called **Henry's Law.**

98. Solubility of Air in Water.—To prove that air dissolves in water, we need only fill a glass from the hot-water faucet in the kitchen. The small air bubbles which separate make the water milky. In a moment they escape and the liquid is clear. The abundance of animal life in water shows that oxygen must dissolve in it. If a globe of goldfish is put under an air pump, so that the dissolved air is taken out of the water, the fish suffocate.

We must now ask another question of the kinetic theory. In what proportions will the nitrogen and oxygen of the air dissolve in water? Will the dissolved air have the same composition as ordinary air, that is, about four-fifths nitrogen to one-fifth oxygen by volume?

First of all, there is no reason to think that the presence of either gas will affect the behavior of the other. We can work out the problem for each gas as though the other were not present.

Since air contains one-fifth of its volume of oxygen, oxygen molecules will strike the surface of the water one-fifth as frequently as if the water was in contact with pure oxygen. 100 c.c. water dissolves, in contact with pure oxygen, 4 c.c. of the gas. In contact with air, it ought to dissolve $\frac{1}{5}$ of 4 c.c., or 0.8 c.c. of oxygen.

For the same reason, the amount of nitrogen dissolved from air ought to be $\frac{4}{5}$ of the volume dissolved when the water is in contact with pure nitrogen. This gives (§96), $2 \times \frac{4}{5} = 1.6$ c.c., for 100 c.c. water. Bunsen found, by direct experiment, that 100 c.c. water dissolved from air 2.47 c.c. of gas, of which 1.61 c.c. was nitrogen and 0.86 c.c. oxygen. The agreement between theory and fact is close.

This is another proof that the air is a mixture. For the calculation we just made is based upon the idea that the nitrogen and oxygen are separate in it. If the air were a compound, it would dissolve unaltered in water and the composition of the dissolved air would be the same as that of the original atmosphere.

99. Avogadro's Hypothesis.—The most striking fact about gases is that they all behave in about the *same way* when pressure or temperature is changed. Each solid and each liquid behaves in its *own* way. The only reasonable conclusion from this is that, in some respect, *the structure of all gases must be alike.* This likeness cannot be in the molecules themselves, for they are composed of different substances, and have, as we shall see, different weights in different gases. The similarity, then, must be in the closeness of packing, in the spacing of the molecules. The average distances between the centers of the molecules in oxygen and nitrogen, for instance, must be the same when the two gases are at the same temperature and pressure. And the molecules in the two gases must approach each other to the same extent for an equal increase of pressure, and must separate to the same extent for an equal increase of temperature, so that the spacing always remains the same, so long as the two gases are at the same temperature and pressure. The same remark applies to all other gases.

Now if the spacing or closeness of packing of the molecules is the same in all gases, under the same conditions, then, at equal temperature and pressure, one liter of all gases must contain the same number of molecules. This statement is called **Avogadro's Hypothesis,** after *Amadeo Avogadro,* who proposed it in 1811. We may put it thus:

Equal volumes of all gases, measured at the same temperature and pressure, contain equal numbers of molecules.

Calculation shows that for a liter of gas at 0° and 760 mm. the number of molecules must be about 3×10^{22}, but in chemistry we are concerned only with its *equality* in different gases, not with the number itself.

100. All the Molecules of the Same Gas Must be Exactly Alike.—Every molecule of oxygen must be exactly like every other, and must have the same weight. For if oxygen contained molecules which differed in size and weight, it would be possible to separate it, by some process of the nature of sifting, into two portions, one of which would contain lighter molecules and be less dense than the other; and other gases could be separated into different specimens in the same way. Elaborate and painstaking attempts have been made to separate various gases into two portions of different densities, and they have always failed.

Definitions

Solid. A body which has a shape, which it retains, unless distorted by external force.

Liquid. A body which takes the shape of the containing vessel, and has a limiting upper surface.

Gas. A body which takes both the shape and the volume of the containing vessel. A gas has no upper surface because it completely fills any vessel in which it is contained.

Density. The quotient obtained by dividing the weight of a body by its volume; the weight of unit of volume.

Molecule. The small particle of a gas which moves about as a whole, during the heat motion of the gas.

Kinetic theory. The theory which explains the properties of gases by the fact that *heat is molecular motion,* so that, at all temperatures above the absolute zero, the molecules are in ceaseless movement.

BOOK II

COMPOUNDS OF OXYGEN

INTRODUCTION

In spite of its importance, the quantity of oxygen in the air is small compared with that which exists in **oxygen compounds.** We shall see that *water* contains eight-ninths of its weight of oxygen. If the earth's surface was perfectly even (a geometrical sphere) the water would cover it everywhere to a depth of about 300,000 cm. (nearly two miles). A layer of water only 264 cm. ($8\frac{2}{3}$ ft.) deep would contain as much oxygen as the atmosphere. Therefore the water on the earth's surface contains more than 1000 times as much oxygen as the atmosphere.

But the quantity of oxygen in the water is trifling compared with the enormous mass which exists, in chemical combination, in the rocks. Calculations based on thousands of analyses show that, on the whole, the materials of which the accessible portion of our planet consists contain about half their weight (49.78%) of oxygen. Oxygen is, therefore by far the most abundant of the elements.

We shall first study, in Chap. VII, the compounds which oxygen forms with the *metals* we have already taken up. Following the same plan, Chap. VIII will be devoted to the oxides of the *non-metallic* elements sulphur and carbon. This will lead naturally in Chaps. IX and X to the study of some minerals which are oxides of elements not yet familiar to us. The concluding chapter of the book will contain an explanation of the method of converting sulphides into oxides by heated air, and oxides into metals by heated carbon. These processes are important in the extraction of metals from their ores.

CHAPTER VII

OXIDES OF FAMILIAR METALS

101. Lead Monoxide.—Melted lead absorbs oxygen and becomes covered with a yellow film of *lead monoxide.* Complete conversion is achieved by steady heating in a furnace where a current of air is drawn over the surface of the liquid metal.

Lead monoxide appears in commerce in two forms. *Litharge* is a mass of yellow-red crystalline scales, used in the making of lead glass. *Massicot* is a dull yellow powder, used in making other lead compounds, especially *red lead.* Both forms are nearly insoluble in water. They turn dark brown when gently heated, and melt readily. They have the same composition, containing for one part of lead, 0.0773 part of oxygen. This could be investigated by weighing out a gram of lead in a porcelain crucible, converting it into lead monoxide and weighing again. The better the balance, and the more careful the work, the more nearly would the weight of the lead monoxide approach 1.0773 gram.

102. Red Lead or "Minium".—When massicot is persistently heated to a very low red heat (500°) in a current of air, it passes into a bright scarlet powder, *red lead.* That *oxygen* is taken up is indicated by the fact that the weight increases. Proof can be obtained by heating the red lead to a higher temperature in a glass tube, when it is again converted into massicot. Oxygen escapes, and can be collected over water and identified by thrusting into it a glowing splint.

Red lead is an oxide of lead which contains more oxygen than lead monoxide. We have seen that the equation

$$\alpha\text{-sulphur} \rightleftharpoons \beta\text{-sulphur}$$

proceeds from left to right at 100° and from right to left at room temperature. This is a similar case. The equation

$$\text{Lead monoxide} + \text{oxygen} \rightleftarrows \text{red lead}$$

proceeds in air from left to right below 550° and from right to left above that point. Red lead, mixed with linseed oil, is much used for painting iron and steel, to protect them against rust.

103. Lead Dioxide.—*Lead dioxide* is a dark brown powder used in storage batteries and in making matches. It is made by treating red lead with nitric acid. Heated in a glass tube, it behaves like red lead; oxygen escapes and lead monoxide is left. The weight of this oxygen can be easily found by gently heating a weighed quantity of lead dioxide in a porcelain crucible. Let us weigh off 1.1546 grams in an uncovered crucible, weighing with it a short glass rod for stirring. Heat gently and stir until the powder has turned completely to yellow lead monoxide. The weight is now 1.0773 grams, .0773 gram of oxygen has escaped.

We have proved, then, that there are:

1 gram of lead + .0773 gram oxygen in lead monoxide.
1 gram of lead + 2 × .0773 gram of oxygen in lead dioxide.

Hence the prefixes *mon-* and *di-*. They are from the Greek numerals for one and two.

104. Iron Monosulphide and Pyrite.—Multiple Proportions.—The law that emerges from these numbers is one of the foundations of our science. Before we put it into words, let us make sure we understand it by calculating another example.

There are two compounds of iron and sulphur. One of them, pyrite, we already know. Its chemical name is *iron disulphide.* The other, *iron monosulphide,* is one of the stock-materials of every laboratory. It is made by heating a mixture of iron and sulphur to redness. In order to find out its composition, let us weigh out a gram of pure iron powder in an uncovered porcelain crucible, add about a gram of sulphur, cover the crucible, and heat until sulphur no longer escapes between crucible and lid. Then we weigh again, without the cover.

The substance is pure iron monosulphide, for the sulphur which did not combine with the iron is vaporized.

The weight of the iron monosulphide is 1.5714 grams.

We know that pyrite loses part of its sulphur when heated. Let us weigh 2.1428 grams of powdered pyrite in an uncovered crucible, cover and heat intensely until no more sulphur escapes, cool, and weigh without the cover. Iron monosulphide remains, and its weight is 1.5714 grams. The sulphur driven off is 0.5714 gram.

1 gram of iron is combined with 0.5714 gram sulphur in iron monosulphide.

1 gram of iron is combined with 2 × 0.5714 gram sulphur in iron disulphide.

Now we can state the law in a general way. **Suppose that two elements A and B form two compounds with each other. Let us consider any fixed weight of A. Then the quantities of B, which are combined with this fixed weight of A in the two compounds, will bear some simple relation to each other.**

Thus, if we take any fixed weight of iron, the sulphur in iron monosulphide bears to the sulphur in iron disulphide the relation of 1:2. If we take any fixed weight of lead, the oxygen in lead monoxide bears to the oxygen in lead dioxide the relation 1:2. The relation is not always 1:2. It may be 1 : 3, 2 : 3, etc., but it can always be expressed by small whole numbers. Thus, if we determine the quantity of oxygen united with one gram of lead in lead monoxide, and also in red lead, we find that the two weights bear the relation 3:4.

This general statement is called the **law of multiple proportions.** The name is a poor one, because the proportions are not always multiple. The essential thing is that *they bear to each other a relation which can be expressed by small whole numbers.*

105. Zinc Oxide.—Only one compound of oxygen with zinc has been obtained. It is called *zinc oxide* and can be made by burning zinc in the air. It is a loose white powder, insoluble in water. It is lemon yellow while hot. Mixed with linseed oil, it is much used as a paint under the name "zinc white." It is not poisonous. Since artificial zinc sulphide is white, zinc oxide paint is not discolored by gases containing sulphur. Zinc oxide is largely employed as a "filler" to mix with the rubber from which automobile tires are made.

106. Compounds of Mercury with Oxygen.—When mercury is allowed to stand exposed to air, small quantities of a black powder called *mercurous oxide* are formed on the surface. It contains 4 grams of oxygen combined with each 100 grams of mercury.

Mercuric oxide contains 8 grams of oxygen for each 100 grams of mercury. Notice the multiple proportion. Notice also the meaning of the terminations *ous* and *ic*. *When there are two oxides of the same element, the termination* **ous** *is often given to the one which contains the smallest percentage of oxygen and* **ic** *to the one which contains the greatest.*

Mercuric oxide is a brick red powder, which turns black when gently heated and recovers its red color on cooling. At the temperature of liquid air (–192°) it has the color of sulphur. We have noted its historical interest and studied its decomposition by heat. We have seen also that mercury, heated close to its boiling-point in air, slowly passes into mercuric oxide. This is too slow to serve as a method of preparation. The oxide is made more quickly by treating mercury with nitric acid and heating the resulting substance to a temperature short of a red heat. Mercuric oxide is slightly soluble in water and, like most mercury compounds, is poisonous. It is used in medicine in ointments for external use.

107. Oxides of Copper.—When sheet copper is heated in air two oxides are formed. Next the copper is a red layer of *cuprous* oxide, and on the outside a black layer of *cupric* oxide. This indicates that cupric oxide is richer in oxygen, since it is formed where the oxygen is more abundant. In fact analysis shows that with 100 parts of copper there are combined

in cuprous oxide 12.6 parts of oxygen
in cupric oxide 25.2 parts of oxygen.

This is another instance of multiple proportions. The law still holds good if we calculate the weights of copper united with a fixed weight of oxygen in the two compounds. Thus, for 100 parts of oxygen, there are

in cupric oxide 396.9 parts of copper
in cuprous oxide 793.8 parts of copper

and these numbers are to each other as 1:2.

Cuprous oxide is a red powder. It is found crystallized in octahedra as the mineral *cuprite*. *Cupric oxide* is black. It is unaltered by ordinary heating, but at the temperature of the electric furnace it separates into oxygen and copper. It has important uses in the laboratory.

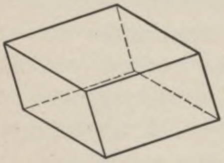

FIG. 26.—A rhombohedral crystal.

108. Oxides of Iron.—The mineral *magnetite* crystallizes in octahedra which are iron-black and yield a black powder, strongly attracted by the magnet. Some specimens are naturally magnetic (lodestone). When pure, it contains 72.40% of iron and 27.60% of oxygen. It is one of the important ores of iron. Great beds of it are found in the Adirondack region, in northern New York, and in the famous iron mines of Sweden.

Hematite crystallizes in **rhombohedrons** (Fig. 26) which have a dark steel-gray color not unlike that of magnetite, but the *powder* is bright red and is not picked up by a magnet. It is the most important iron ore and is found in enormous deposits in northern Minnesota, Michigan and Wisconsin. About fifty million tons of hematite are mined each year in this region.

When pure, hematite contains 70% of iron and 30% of oxygen. Its chemical name is *ferric oxide* (from the Latin *ferrum*, iron). Large quantities of ferric oxide are made artificially. It is used as a polishing powder for glass and metals and as a cheap paint for freight cars, roofs, barns and fences. The red color of bricks and earthenware is due to small quantities of ferric oxide.

The oxide formed when iron burns in oxygen has the same composition as magnetite. The black scales that fall from iron under the blacksmith's hammer resemble magnetite, but they seem to contain some unburnt iron mixed with the oxide, for their composition varies.

Limonite is also an important iron ore. It is found not in crystals, but in masses which are black and lustrous on the surface, but brown in the interior. It is found in Connecticut and New York near the boundary of the two states, in Pennsylvania and elsewhere in the eastern U.S. It is used as a brown paint.

When dry limonite is heated in a dry test tube, *water* appears in the upper part of the tube and ferric oxide is left. The proportions of water and ferric oxide from pure limonite are always the same. It follows that limonite is a *compound* of ferric oxide and water. Like elements, compounds may unite to form more complex compounds in which their properties are completely lost.

109. Oxides of the Precious Metals, Gold, Platinum and Silver.—Since the precious metals are not acted upon by air, even at a red heat, it is clear that their oxides are not easily formed by direct combination. On the contrary the oxides separate easily into oxygen and metal at a gentle heat or even in the cold, under the influence of light. The oxides of gold and platinum are black or brown powders, which lose their oxygen so readily that they are difficult to prepare.

110. Silver Oxide.—When silver powder is heated to 300° in pure oxygen at a pressure of 20 atmospheres (20 × 760 mm.) the two elements combine to form silver oxide. This is a brown powder, which can be more easily made by other methods. In *air* the pressure of the oxygen is 760 mm. $\times \frac{1}{5}$ or about 150 mm. *Now in air at* 300° *silver oxide loses its oxygen completely, leaving a lustrous mossy residue of silver.* It appears, therefore, that the change

$$\text{Silver} + \text{oxygen} \rightleftharpoons \text{silver oxide}$$

can be made to travel either forward or backward, at the same temperature, by simply altering the closeness of packing (**concentration**) of the oxygen. When the concentration of the oxygen is high it unites with the silver; when it is low, the silver oxide separates.

This influence of the concentration of the reacting substances upon the progress of a chemical change is one of the most important things we have to understand. First, let us get a clear idea of what concentration means. It is the closeness with which a substance is packed—the quantity of it in 1 c.c. of the space in which the chemical change takes place. In the above example the concentration of the oxygen is stated in terms of pressure, because, according to Boyle's law, concentration in gases is proportional to pressure and is measured by it (p. 65). In pure oxygen, at 20 atmospheres, the pressure of the oxygen is just about 100 times as great as it is in air at 1 atmosphere. But the essential thing is not that the pressure of the oxygen is 100 times as great, but that 100 times the oxygen is crowded into 1 c.c. This means that 100 times as much oxygen is offered to the silver by the gas in contact with it. Naturally, this favors the production of silver oxide.

We have shown that, in pure oxygen, combustions are much more energetic than in air. The reason is simply that, in pure oxygen, the concentration of the oxygen is five times as great.

111. Percentage Composition of Important Oxides and Sulphides.—The following tables give the percentage composition of some important oxides and sulphides. Only one of the substances is new to us. This is *cupric sulphide*. The compound of copper and sulphur which we have made and studied is called *cuprous* sulphide. *Cupric* sulphide contains twice as much sulphur, combined with the same weight of copper. It is a dark blue mineral found on lava at Vesuvius, in Chili and elsewhere.

Sulphides	Oxides
1. Lead sulphide 13.39% sulphur 86.61% lead	2. Lead monoxide 7.18% oxygen 92.82% lead
3. Mercuric sulphide 13.79% sulphur 86.21% mercury	4. Mercuric oxide 7.41% oxygen 92.59% mercury
5. Zinc sulphide 32.82% sulphur 67.18% zinc	6. Zinc oxide 19.63% oxygen 80.37% zinc

SULPHIDES	OXIDES
7. Cupric sulphide 33.51% sulphur 66.49% copper	8. Cupric oxide 20.13% oxygen 79.87% copper
9. Cuprous sulphide 20.13% sulphur 79.87% copper	10. Cuprous oxide 11.19% oxygen 88.81% copper
11. Silver sulphide 12.90% sulphur 87.10% silver	12. Silver oxide 6.90% oxygen 93.10% silver
13. Iron monosulphide 36.36% sulphur 63.64% iron	14. Magnetite 27.59% oxygen 72.41% iron
15. Iron disulphide 53.33% sulphur 46.67% iron	16. Ferric oxide 30.00% oxygen 70.00% iron

112. Discussion of the Table.—This table contains a mass of information, but it is in a form in which it could not be used with comfort and could not be remembered at all. Looking through the column of oxides, we fail to discover any relation between the numbers expressing the quantities of oxygen in them. There is the same absence of connection between the quantities of sulphur in the eight sulphides given in the table.

Now let us take the first plain step in the direction of simplifying matters. Let us choose some fixed quantity of oxygen and calculate the quantity of the metals combined with it in the oxides. The standard quantity of oxygen, chosen by the chemists of the world, is **16 grams.** The reasons for the choice of the number 16 will appear later. The calculation is made by proportion.

For lead monoxide (2) $7.18 : 92.82 :: 16 : x \therefore x = 207$
For mercuric oxide (4) $7.41 : 92.59 :: 16 : x \therefore x = 200$
For zinc oxide (6) $19.63 : 80.37 :: 16 : x \therefore x = 65.5$
For cupric oxide (8) $20.13 : 79.87 :: 16 : x \therefore x = 63.5$

113. Calculations Based upon the Table.—This device rids us of half the numbers in the table of oxides, for if the quantity of oxygen is the same in all, we have only to remember the quantity of metal. We might re-calculate the composition of the sulphides in a similar way, by choosing some fixed weight of sulphur and so simplify the sulphide table.

But need the choice of the standard weight of sulphur be arbitrary? Are we, in fact, free to choose it at all? Does it not follow from the choice we have already made, of 16 grams of oxygen as a basis? Sixteen grams of oxygen combine in lead monoxide with 207 grams of lead. What quantity of sulphur combines with 207 grams of lead?

This question is answered at once by a proportion based on the figures given in (1).

$$86.61 : 13.39 :: 207 : x \therefore x = 32$$

This quantity of 32 grams of sulphur is related in a very real way to the standard quantity of 16 grams of oxygen—*they both combine with the same weight of lead.* So far as lead is concerned 32 *grams of sulphur will take the place of, or are equivalent to,* 16 *grams of oxygen.*

Therefore we have a good reason for using 32 grams of sulphur as a basis for our re-calculation of the table of sulphides. How much mercury will combine with 32 grams of sulphur? From (3) we construct the proportion

$$13.79 : 86.21 :: 32 : x \therefore x = 200.$$

This surprising result is of the greatest importance. The same 200 grams of mercury which combine with the standard quantity of oxygen (16 grams) also combine with the standard quantity of sulphur (32 grams).

From (5) we calculate the quantity of zinc which combines with 32 grams of sulphur

$$32.82 : 67.18 :: 32 : x \therefore x = 65.5$$

This is the same weight of zinc which we found in zinc oxide, combined with 16 grams of oxygen.

For copper, we have from (7)

$$33.51 : 66.49 :: 32 : x \therefore x = 63.5$$

Again we get the same quantity which combined with 16 grams of oxygen.

So far as the compounds from (1) to (8) inclusive are concerned the following holds good: that we have assigned a number to each element, and that we can write the composition of any one of the eight compounds by simply setting down the numbers corresponding to the elements it contains.

114. The Composition of Chemical Compounds.—Recalling the fact of multiple proportions (p. 80) we may conjecture that it will often be necessary to *multiply* these standard quantities by small whole numbers in order to write the composition correctly. For instance, cuprous oxide contains twice as much copper, for the same weight of oxygen, as cupric oxide (p. 85). If cupric oxide contains one standard quantity each of oxygen and copper, then cuprous oxide must contain one standard weight of oxygen combined with two standard weights of copper. In fact by proportion we obtain from (10):

$$11.19 : 88.81 :: 16 : x \therefore x = 127 \text{ grams}$$

for the weight of copper combined with 16 grams of oxygen in cuprous oxide. 127 is 63.5×2 or twice the standard quantity of copper.

For the quantity of copper combined with 32 grams of sulphur in cuprous sulphide we get from (9):

$$20.13 : 79.87 :: 32 : x \therefore x = 127 \text{ or } 63.5 \times 2.$$

So that cuprous sulphide contains two standard quantities (63.5 grams × 2) of copper combined with one standard quantity (32 grams) of sulphur.

There are about 60 metals and we might have included them all in our table. The amount of calculation would have been greater, but the results would have been similar. We would have obtained a number for each metal, and by means of these numbers the composition of the oxides and sulphides of the metals could have been written.

Fifteen non-metallic elements are known and if we had included them with all of the metals, our table would have covered the whole field of chemical science, with the exception of the elements of the argon group (p. 59), which form no compounds. We should have obtained for each element a figure which, multiplied when necessary by small whole numbers, would express the quantity in which it entered into all its compounds, provided that the quantities of the other elements were also expressed by the numbers which we had assigned to them.

Such a complete system of numbers is given in the table on the inside of the back cover. The numbers are called **atomic weights** for reasons we shall discuss later. The meaning of the table is that *the composition of every chemical compound can be expressed by the numbers in it, multiplied where necessary.* Thus, suppose that a new compound is prepared, which is proved to contain nothing but nitrogen and sulphur. We know beforehand that the quantity of nitrogen in it must be $14 \times x$ and the quantity of sulphur $32 \times y$ where x and y are small whole numbers, not often as great as five. So the problem of expressing its composition becomes the simple one of finding what small multiples of the standard weights are required.

115. Symbols and Formulas.—*The symbols given in the table indicate the atomic weights of the elements.* Thus S means not merely sulphur, but a *special quantity of sulphur, 32 grams.* In the same way O indicates 16 *grams of oxygen* and Zn 65.5 *grams of zinc.* We should avoid using these symbols as though they were merely abbreviations of the names, and learn to connect with them the idea of a definite quantity by weight, different for each substance.

The numbers should not be memorized. They will grow familiar by use. The values given in the column headed "approximate" are to be used in solving all problems. Those elements which are important enough to be studied in detail are in italics in the tables. The others are rare and will be considered briefly or not at all.

Remember, however, that from the standpoint of pure science—*which is, in the long run, the only truly practical standpoint*—a rare element is a distinct form of matter, and is just as interesting to the chemist as a common one. Also the mere fact that an element is not abundant does not mean that it is useless. Great progress has been made of late in the utilization of the rare elements, and substances like thorium, cerium, tungsten and tantalum are the raw materials of great industries. The scientific curiosity of one decade is the necessity of the next.

116. Uses of the Symbols.—The symbol is the first letter of the name of the element. A second letter is added where confusion with some other symbol would result if only one letter was used. Thus, for silicon Si is used, because S is already taken for sulphur. The symbols are the same in all languages. In some cases it happens, especially with familiar metals, that the name begins with different letters in different languages. In order to preserve the international character of the system, the symbol is then made from the Latin name. A reference to the table will show that this has been done with iron, gold, lead and other metals.

In expressing the composition of compounds, the symbols of the elements are placed together. Thus *lead monoxide* contains one atomic weight (207 grams) of lead, combined with one atomic weight (16 grams) of oxygen. Its composition is therefore given by the expression PbO. This is called the **formula** of lead monoxide. *Lead sulphide,* which contains one atomic weight each of lead and sulphur, receives the formula PbS. The formula of *cupric oxide* is CuO for the same reason. But *cuprous oxide,* which contains two atomic weights of copper to one of oxygen, has the formula Cu_2O. In the same way *cupric sulphide* is CuS and *cuprous sulphide* Cu_2S. Notice that a symbol is multiplied by a small figure placed after it and below. *This figure multiplies only the symbol which immediately precedes it.*

117. Calculation of the Percentage Composition.—The formula PbO means that lead monoxide contains 207 parts of lead and 16 parts of oxygen in $207 + 16$ or 223 parts.

The *percentage* of lead must be

$$\frac{207}{223} \times 100 = 92.82$$

that of oxygen $\frac{16}{223} \times 100 = \underline{7.18}$

$$100.00$$

In cuprous sulphide there are $63.5 \times 2 = 127$ parts of copper and 32 parts of sulphur, making 159 parts in all.

The percentage of copper is $\frac{127}{159} \times 100 = 79.87,$

that of sulphur $\frac{32}{159} \times 100 = \underline{20.13}$

$$100.00.$$

The term *atomic weight* applies cnly to elements. There is no such thing as the atomic weight of a compound. The sum of the atomic weights of the symbols in the formula is called the **molecular weight.** 223 is the molecular weight of lead monoxide (PbO) and 159 is the molecular weight of cuprous sulphide (Cu_2S).

118. Calculation of the Formula from the Percentage Composition.— In fixing the formula of a compound, its composition must first be determined by methods similar in principle to those we employ in the laboratory. Thus by heating a weighed quantity of silver with sulphur in a covered porcelain crucible, and weighing the silver sulphide produced, we could show that it contained

12.90% of sulphur
87.10% of silver

Our problem is to express the quantity of sulphur in terms of the atomic weight of sulphur and that of silver in terms of the atomic weight of silver (108).

$12.90 \div 32 = .406$
$87.10 \div 108 = .806$

Now $.406 : .806 :: 1 : 2$

Therefore silver sulphide contains two atomic weights of silver to one of sulphur and its formula is Ag_2S.

Hematite contains

30.00% oxygen
70.00% iron
$30 \div 16 = 1.875$

The atomic weight of iron (see table) is 56

$$70 \div 56 = 1.25$$
$$1.25 : 1.875 :: 2 : 3$$

The formula of Hematite (ferric oxide) is Fe_2O_3.
Magnetite contains

$$27.59\% \text{ oxygen}$$
$$72.41\% \text{ iron}$$
$$27.59 \div 16 = 1.724$$
$$72.41 \div 56 = 1.293$$
$$1.293 : 1.724 :: 3 : 4$$

The formula is Fe_3O_4.

The student should have no difficulty in proving the formulas of cinnabar, zinc blende and pyrite from the percentages given on pp. 84, 85.

119. Formulas of the Oxides and Sulphides already Studied.—The following table gives the formulas of the oxides and sulphides already studied.

Sulphides		*Oxides*	
Lead sulphide	PbS	Lead monoxide	PbO
Mercuric sulphide	HgS	Red lead	Pb_3O_4
Zinc sulphide	ZnS	Lead dioxide	PbO_2
Cupric sulphide	CuS	Mercuric oxide	HgO
Cuprous sulphide	Cu_2S	Mercurous oxide	Hg_2O
Chalcopyrite	$CuFeS_2$	Zinc oxide	ZnO
Silver sulphide	Ag_2S	Cupric oxide	CuO
Iron monosulphide	FeS	Cuprous oxide	Cu_2O
Pyrite	FeS_2	Silver oxide	Ag_2O
		Ferric oxide	Fe_2O_3
		Magnetite	Fe_3O_4

120. Equations.—Mercuric oxide is decomposed by heat:

$$\text{Mercuric oxide} \longrightarrow \text{mercury} + \text{oxygen.}$$

Using our symbols, this becomes:

$$HgO \longrightarrow Hg + O.$$

This equation has a precise quantitative meaning. It means that 216 grams of mercuric oxide will yield 200 grams of mercury and 16 grams of oxygen. Problems relating to the amount of oxygen which can be obtained from a given weight of mercuric oxide can be solved at once from the equation. What weight of oxygen can be obtained from 27 grams of mercuric oxide? The solution is

$$\frac{16}{216} \times 27 = 2 \text{ grams of oxygen.}$$

If we want the *volume* of the oxygen in liters we have only to divide 2 grams by the weight of 1 liter of oxygen (p. 54) 1.43 grams.

$$2 \div 1.43 = 1.4 \text{ liters at } 0^\circ \text{ and } 760 \text{ mm.}$$

How much mercuric oxide is needed to make 20 grams of mercury? The solution is

$$\frac{216}{200} \times 20 = 21.6 \text{ grams of mercuric oxide.}$$

Definitions

Storage battery. An electric battery which, when exhausted, can be charged, by connecting it with a dynamo, and used again and again as a source of electric current.

Rhombohedron. A crystal bounded by six equal rhombic faces (Fig. 26).

Concentration. The closeness with which a substance is packed; the quantity of a substance in unit of volume. For instance, the concentration of oxygen is greater in pure oxygen than in air, and still greater in compressed oxygen.

Atomic weight. (1) The *quantity,* in grams, in which an element enters into its compounds. (2) The weight of the *atom* of an element, if the value 16 is *assigned* to the weight of the atom of oxygen.

Symbol. The first letter or the first two letters of the name of an element. It means: (1) the *atomic weight* of the element, taken in grams; (2) the *atom* of the element.

Formula. (1) A group of symbols which gives the *composition* of a substance in parts by weight. (2) A group of symbols which represents the *molecule* of a substance, each symbol representing an atom.

CHAPTER VIII

OXIDES OF NON-METALS ALREADY STUDIED: SULPHUR DIOXIDE, SULPHUR TRIOXIDE, CARBON DIOXIDE, CARBON MONOXIDE, CARBON SUBOXIDE

121. Sulphur Dioxide.—We have noted (p. 55) that sulphur burns in oxygen, yielding a colorless gas with an irritating smell. Since both substances are elements, this can only be a case of combination. The gas produced is called *sulphur dioxide*, because it contains two atomic weights of oxygen. It can be obtained in a fairly pure state by means of the apparatus shown in Fig. 27. The sulphur in the bulb is gently heated. A slow current of oxygen comes from a cylinder of the compressed gas. Sulphur dioxide cannot be collected over water, for one volume of water dissolves about 50 volumes of it at room temperature. Being more than twice as dense as air, it is collected by running it into the bottom of a dry cylinder, so that the air is forced out at the top.

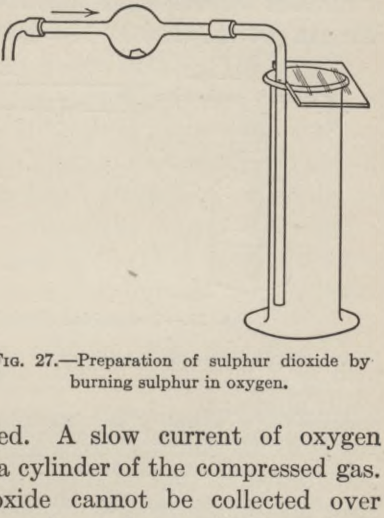

Fig. 27.—Preparation of sulphur dioxide by burning sulphur in oxygen.

Fig. 28.—Proof that oxygen yields its own volume of sulphur dioxide.

122. Sulphur Dioxide Contains its own Volume of Oxygen.—An important fact about the burning of sulphur can be learned from the experiment shown in Fig. 28. The retort is filled with oxygen and dips into mercury, the level of which is slightly higher inside to allow for some expansion of the oxygen by heat. The bit of sulphur at A is heated gently till it burns. At first the expansion due to heat drives the mercury down a little, but, when the retort cools, the level is the same as at first. *The oxygen has produced its own volume of sulphur dioxide.* When oxygen combines with sulphur the relation, by volume, of the oxygen to the sulphur dioxide is 1 : 1.

123. Quantities by Weight.—Let us now consider the quantities *by weight* in which oxygen and sulphur unite. We can predict that 32 × x grams of sulphur will combine with 16 × y grams of oxygen, and that x and y will be small whole numbers.

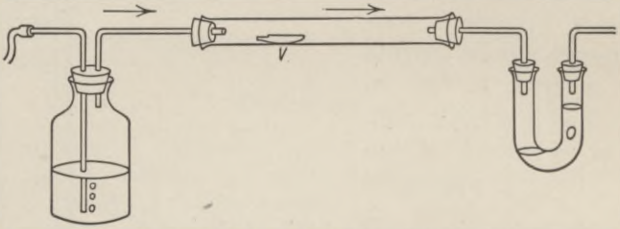

FIG. 29.—Composition of sulphur dioxide by weight.

Information about the values of x and y can be obtained by the experiment shown in Fig. 29. A gentle stream of oxygen is passed through the apparatus in the direction indicated by the arrows. A weighed quantity of sulphur is burned in the little porcelain vessel V, and the sulphur dioxide is all absorbed by a strong solution of potash lye (chemical name *potassium hydroxide*), placed in the U-shaped tube, which is weighed before and after the experiment. If one gram of sulphur is taken, it is found that the increase in weight of the U-tube is 2 grams. This means that 2 grams of sulphur dioxide have been formed:

1 gram sulphur unites with 1 gram oxygen, therefore 32 grams (1 atomic weight of sulphur) unite with 32 grams (2

atomic weights) of oxygen. Therefore, if $x = 1$, $y = 2$, or, the formula of sulphur dioxide is SO_2.

There is one thing taken for granted in this reasoning: that $x = 1$, that is, that there is really one atomic weight of sulphur in sulphur dioxide. Our experiment shows only that

$$x : y :: 1 : 2.$$

Thus if there were 2 atomic weights of sulphur in sulphur dioxide, there would be four of oxygen and the formula would be S_2O_4. Since this represents exactly the same proportions by weight of the two elements as the formula SO_2, our experiment does not decide between the two.

The reasons for regarding SO_2, and not some multiple of it, as the correct formula, will be given later. In the meantime, notice the general fact that the simplest formula answers most purposes of practical calculation, especially by weight. For instance, in calculating how much sulphur must be burned to yield a desired weight of sulphur dioxide, it makes no difference whether the formula SO_2, or some multiple of it, is taken as a basis.

124. Properties and Uses.—Sulphur dioxide is more easily condensed than most other gases. At −8°, under atmospheric pressure, or at room temperature (20°) under a pressure of 3¼ atmospheres, it becomes a colorless liquid which is sold in iron cylinders, or in siphon bottles of glass or metal, and is used in bleaching wool and silk. This liquid absorbs much heat when it evaporates and has been used as the working liquid in one kind of ice machine. However, the ammonia machine (Chap. XIII) is the usual type.

Sulphur dioxide is an excellent disinfectant, and was formerly much used for this purpose, but, on account of its destructive action on colored fabrics and metal surfaces, it has been displaced by *formaldehyde* (Chap. XIV). It is poisonous to animals, but its odor gives warning of its presence and accidents with it rarely occur. It is much more dangerous to plants. Even traces of it in the air have a most injurious effect upon vegetation. This is especially true of evergreen timber, like pine, hemlock and spruce.

The great use of sulphur dioxide is for the preparation of sulphuric acid, the most important of all non-metallic chemical products. For this purpose, sulphur dioxide is made by burning pyrite, FeS_2, which is far cheaper than sulphur.

125. Sulphur Trioxide.—*Sulphur trioxide,* SO_3, is made by the union of sulphur dioxide with another atomic weight of oxygen.

$$SO_2 + O \rightleftarrows SO_3$$

This combination is very slow, but in the presence of finely divided platinum or of ferric oxide it becomes, at 400°, rapid enough to serve as the basis for the commercial production of the trioxide.

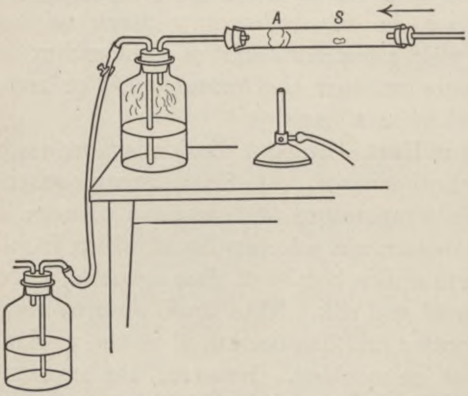

FIG. 30.—Formation of sulphur trioxide from sulphur dioxide and oxygen.

Fig. 30 shows a lecture-table illustration of the formation of sulphur trioxide. Sulphur burns at *S*. By running water out of the upper bottle, enough air is drawn over the sulphur to provide an excess of oxygen. At *A* is a wad of asbestos which has been coated with finely divided platinum. When this is gently heated, a dense white cloud of sulphur trioxide appears in the bottle, where it is slowly absorbed by the water.

126. Catalytic Action.—In this experiment the platinum remains unchanged. If it was consumed in the reaction, the method could not be used commercially, since platinum is very expensive, much more so than gold. The function of the platinum is merely to *hasten* a process *which would take place without its aid,* if time enough were allowed.

Cases of this kind, in which a substance alters the speed of a change, without seeming to enter into it as one of the reacting substances, are numerous, as we shall see. They are of special interest from the practical point of view, because, since the substance acting in this way is not consumed, the best material for the purpose can be employed, no matter how costly. A special noun, **catalysis,** has been coined as a class name for action of this sort. The corresponding adjective is **catalytic,** and the substance is called the **catalyzer.** The term **contact action** is often used with the same meaning as catalysis. The preparation of sulphur trioxide on a large scale by the method we have just discussed is called the **contact process.**

127. Properties of Sulphur Trioxide.—Sulphur trioxide is sold sealed up in glass bulbs. It is a mass of pure white, silky needles, resembling asbestos. When exposed, it gives off a dense, white, suffocating smoke, and absorbs water from the air, passing into a colorless, oily liquid which is *sulphuric acid.* The chief use of sulphur trioxide is for the preparation of sulphuric acid (Chap. XX). It reacts with water so violently that great care must be taken in bringing the two together.

In the production of sulphur trioxide, two volumes of sulphur dioxide unite with exactly one volume of oxygen. The reaction is reversible, as the arrows indicate (§125). If sulphur trioxide is heated to 900°, it separates completely into the dioxide and oxygen. Even at 700° about 40% of it is decomposed. For this reason, the temperature must be maintained carefully at 400°.

128. Soda Water.—When *soda water* runs into the glass, the rapid rise of bubbles to the surface shows that a gas is escaping. A siphon bottle of soda water affords a means of collecting some of this gas (Fig. 31). A rubber tube is slipped over the nozzle and the bottle inverted. The gas is collected over water, though there will be some loss by solution. It proves to be colorless and odorless, but it has a sharp, pungent taste—the refreshing flavor of effervescing drinks is due to it, the taste being modified by the presence of other materials. A flame lowered into the gas is extinguished as though dipped into water.

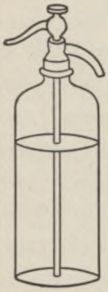

FIG. 31.—A siphon bottle for soda water.

Limewater is a colorless liquid, used in medicine. It is made by slaking a little lime with much water, and pouring off the clear liquid, after the excess of slaked lime has settled. A little limewater, poured into a bottle of the soda-water gas, at once becomes cloudy; a white solid containing lime has separated in the liquid. Since no other gas, which could well be confused with it, gives this result, we may use the reaction with limewater as a *test* for the soda-water gas.

129. Composition of Carbon Dioxide.—We heat a piece of *charcoal* in a spoon and lower it into a jar of oxygen. Energetic combustion gives evidence of a chemical change. This can only be a *combination* of the two substances, since both are elements. When it is over, some or all of the charcoal has disappeared and the jar contains an invisible gas which renders limewater cloudy and extinguishes flame. The same gas which escapes from soda water is formed by the burning of charcoal in oxygen. Graphite and diamond burn in oxygen to the same gas, and equal weights of charcoal, graphite and diamond form equal weights of the compound. This is a final proof that charcoal, graphite and diamond are three forms of the same element, *carbon.* The gas formed is called *carbon dioxide.*

130. Formula of Carbon Dioxide: Volumetric Method.—There are two ways of getting quantitative knowledge: by measuring volumes (volumetric method), and by working with weighed quantities and weighing the products (gravimetric method). We had examples of both under sulphur dioxide (pp. 94, 95).

Let us try the volumetric method first. Like sulphur, carbon combines with oxygen without changing the volume of the latter—the volume of the carbon dioxide is equal to that of the oxygen used up. This can be shown by the apparatus illustrated in Fig. 32. The vessel contains oxygen, confined by mercury in the narrow lower part. The platinum wires which pass through the glass are connected by a spiral of platinum wire in which is slipped a stick of charcoal. An electric current, sent through the spiral, heats it red-hot and sets fire to the charcoal. When the apparatus is cold, the level of the mercury is the same as it was before the combustion.

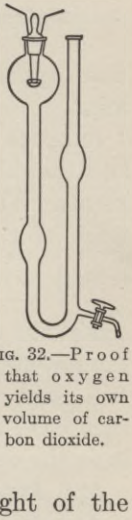

FIG. 32.—Proof that oxygen yields its own volume of carbon dioxide.

Accordingly, a liter of oxygen, if enough charcoal was burned in it, would form a liter of carbon dioxide. We have seen that the weight of a liter of oxygen is 1.429 grams. The weight of a liter of carbon dioxide is 1.965 grams. The difference, 0.536 gram, is the weight of the carbon. Now the atomic weight assigned to carbon by an extensive study of carbon compounds is 12. How much oxygen is combined with this weight of carbon in carbon dioxide?

$$0.536 : 1.429 :: 12 : x \therefore x = 32.$$

Since O = 16, the formula is CO_2.

131. Gravimetric Method.—The gravimetric method confirms this. The principle is exactly the same as that of the experiment in which we determined the composition of sulphur dioxide (Fig. 29). The apparatus is shown connected, in Fig. 33, and an enlarged view of the vessel (potash bulb) used for absorbing the carbon dioxide is shown in Fig. 34. The gas passes through it from left to right. The lower bulbs are half-filled with a strong solution of potash lye (chemical name *potassium hydroxide*), which absorbs the carbon dioxide completely. The absorption apparatus is weighed before and after the experiment.

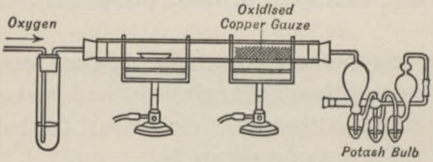

FIG. 33.—Composition of carbon dioxide by weight.

Suppose that 1 gram of pure charcoal has been burned, and that the increase in weight of the potash bulb is 3.667 grams. Then 2.667 grams of oxygen have united with 1 gram of carbon.

$$1 : 2.667 :: 12 : x \therefore x = 32$$

Again the simplest formula is CO_2. Our proof rests upon the statement that C = 12, which we have taken for granted. We shall consider later the proof that CO_2, and not some multiple of it, is the correct formula.

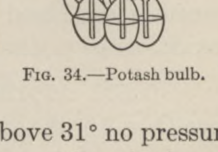

FIG. 34.—Potash bulb.

132. Properties of Carbon Dioxide.—At −79° carbon dioxide passes, under a pressure of one atmosphere, into a colorless liquid of about the density of water. At 0°, 35 atmospheres are required to liquefy it; at room temperature (20°), 60 atmospheres; and at 31°, 70 atmospheres. Above 31° no pressure, however great, will produce liquefaction, although the gas may be compressed into a smaller volume than the liquid would occupy at a lower temperature. 31° is called the

critical temperature of carbon dioxide. It is the highest temperature at which the gas can be liquefied.

Each gas has its critical temperature, above which it cannot be changed into a liquid. For oxygen, this temperature is –118°. Before this was understood, pressures up to 3000 atmospheres were applied to oxygen at room temperature, in unsuccessful attempts to liquefy it. The critical temperature of nitrogen is –146°, so that, like oxygen, it requires great cold, along with pressure, to liquefy it. On the other hand, the critical temperature of sulphur dioxide is high (155°), and it is easily liquefied by pressure alone at ordinary temperatures.

When a cylinder of liquid carbon dioxide is opened, the liquid rushes out, and at once evaporates. This produces such intense cold, that a portion of it is frozen to a solid, which resembles snow. Solid carbon dioxide has a temperature of –80°. It may be placed lightly on the hand or tongue without danger, but, if squeezed into close contact, freezing of the flesh and injury result. Mixed with alcohol or ether it makes a powerful freezing mixture.

133. **Uses of Carbon Dioxide.**—Liquid carbon dioxide is sold quite cheaply in strong steel cylinders. These cylinders are employed in charging soda water and other drinks with the gas. At Saratoga, N. Y., and elsewhere, the carbon dioxide which streams from the earth is collected and liquefied by compression pumps. The gas is one product of fermentation, and the great quantities which are formed in the fermenting cellars of breweries are often utilized. Carbon dioxide is an excellent fire extinguisher, and it has been proposed to distribute the liquid in cities by systems of pipes, just as is now done with water, and have it ready everywhere for this purpose, but the suggestion has never been followed.

134. **Sources of Carbon Dioxide.**—Carbon dioxide is contained in the gases from volcanoes. Large quantities of the gas issue from the earth in some localities. Near Naples is

a cave called the *Grotto del Cane*, which has a depression about two feet deep in the floor. This sunken portion is kept full of carbon dioxide by a natural outflow. Dogs which venture into it are suffocated, while a man walks about unharmed, because his head is above the level of the dense gas. Death Valley, in Java, is a little wooded hollow in which many wild animals are killed in the same way.

About a billion tons of coal are mined and burned each year. That carbon dioxide is formed by the burning can be proved by sucking out some of the gas from the smoke pipe of a furnace in such a way that it bubbles through limewater. From the equation

$$C + O_2 \longrightarrow CO_2,$$

making the assumption that coal contains, on an average, 75% of carbon, we can make a rough estimate of the weight of carbon dioxide thrown into the air each year from this source.

$$1 \times 0.75 \times \frac{44}{12} = 2\tfrac{3}{4} \text{ billion tons.}$$

The fact that limewater becomes cloudy when we blow through it by means of a glass tube proves that carbon dioxide is contained in the gas from the lungs (4.4% by volume). It is impossible to make an estimate of the amount of carbon dioxide which gets into the atmosphere from the breathing of animals, but the quantity must be very great. Each man, for instance, produces about 800 grams of it per day, and the population of the world is nearly 15×10^8. This means a yearly production of nearly 220 million tons (metric) by the respiration of the human race alone.[1]

135. The Carbon Dioxide of the Atmosphere.—To these prodigious quantities of carbon dioxide cast into the atmosphere we must add unknown but very large amounts for the respiration of the lower animals and the higher plants, for

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[1] The metric ton is 2204 lbs. In these rough calculations it may be taken as equal to the avoirdupois ton.

plants continually give off small quantities of the gas. It is a product of the decay of animal and vegetable matter, and the amount which gets into the air from this source must be very great. We must recall also the carbon dioxide of volcanic gases and the constant streams of it which escape in certain localities, like those mentioned in the two preceding sections.

The total quantity of carbon dioxide in the atmosphere is enormous. But the weight and volume of the atmosphere are so immense that the *percentage* of carbon dioxide is small (.03% by volume or 3 parts in 10000). Since this percentage *does not increase* there must be some process in operation which takes the carbon dioxide out of the air about as fast as it enters from the sources just mentioned. How this removal of carbon dioxide is effected is shown by the experiment illustrated in Fig. 35.

The flask contains sprigs of fresh mint, covered with water which has been saturated with carbon dioxide. The test tube is filled with the same liquid. Nothing happens in the dark, but in sunlight bubbles of gas rise and collect in the test tube. The spark test shows that the gas is *oxygen*. That the oxygen comes from the carbon dioxide can be proved by using water freed from dissolved gases by boiling. Under these conditions, no oxygen is formed. The water merely serves the purpose of making it easy to collect the oxygen.

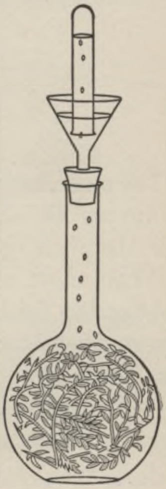
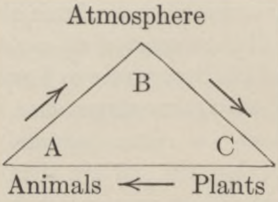


FIG. 35.—Formation of oxygen with leaves of plants.

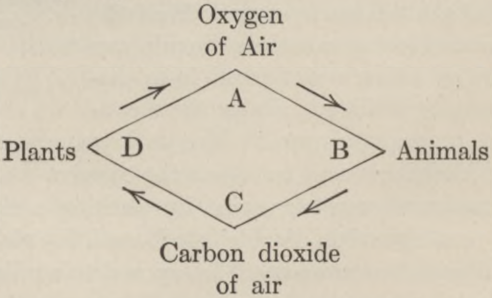
The experiment can be varied by packing a flask with mint and passing carbon dioxide into it until the air is all expelled. When the arrangement is exposed to sunlight, oxygen is formed, which can be separated from the carbon dioxide by a solution of potash lye (potassium hydroxide) which absorbs the latter. Other fresh green leaves can be used, instead of mint, in both experiments.

136. The Cycle through Which Oxygen Passes.—These results show that, in sunlight, the green leaves of plants decompose carbon dioxide and return the oxygen to the air. The carbon is built up into complex compounds which ultimately form the structure of the plant. We may represent the stages through which the *carbon* passes in nature by a triangle:



The meaning is that the carbon of the animal body is oxidized into carbon dioxide and cast into the air. Thence the carbon is absorbed by plants, which build it up into their tissues. When these are eaten by animals, the cycle begins anew. After the death of an animal or a plant, the carbon is converted into carbon dioxide during decay, and returned to the atmosphere.

The cycle through which *oxygen* passes in nature can be represented by a quadrilateral.



This means that the oxygen of the air is taken up by animals who cast into the atmosphere a liter of carbon dioxide for every liter of oxygen which they consume. This carbon dioxide is decomposed by the plants, which return the oxygen to the air, and the cycle begins again. It is probable, though far from certain, that the plants restore to the atmosphere just about as much oxygen as the animals (including man) remove from it by combustion and respiration. Fairly exact analyses of the air have been made for the last seventy-five years, but they have not shown any permanent change in the percentages of oxygen or of carbon dioxide. Air which had been sealed up in vases in the ruins of Pompeii for nearly two thousand years proved, when examined by Liebig, to have the same composition as the present atmosphere.

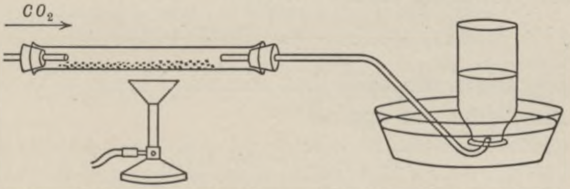


FIG. 36.—Action of heated zinc on carbon dioxide.

137. Action of Carbon Dioxide upon the System.—Carbon dioxide is not poisonous. The workmen in the fermenting cellars of breweries continually breathe air containing 2% or more without damage: 5% is injurious and much more than that rapidly causes death by suffocation. When the body is plunged into a vessel containing carbon dioxide, the head being left free so that pure air is inhaled, there is at first a tingling sensation of warmth over the skin. This is followed by such alarming collapse that the experiment must be discontinued.

138. Carbon Monoxide, CO.—When burning magnesium is lowered into a jar of carbon dioxide, the combustion continues and white magnesium oxide mixed with carbon (lampblack) is produced. But when a stream of carbon dioxide is passed over hot zinc dust, Fig. 36, the zinc turns to white zinc oxide, but no lampblack separates. Instead, a colorless gas issues from the tube and can be collected over water, in which it is very slightly soluble. This gas does not render limewater turbid, so it is not carbon dioxide. When a flame is applied, the gas takes fire and burns with a blue flame, exactly like that which plays over the surface of a coal fire. The product of the burning is carbon dioxide, for the contents of the vessel after the flame has died out render limewater white and opaque.

The zinc has removed half of the oxygen from the carbon dioxide, producing *carbon monoxide*, CO:

$$CO_2 + Zn \longrightarrow ZnO + CO,$$

and the carbon monoxide has combined again with oxygen when the flame was applied:

$$CO + O \longrightarrow CO_2.$$

Carbon monoxide would also have been obtained if the tube had contained red-hot charcoal instead of zinc:

$$CO_2 + C \longrightarrow 2CO.$$

This last reaction occurs in a coal fire. Next the grate, where the air supply is abundant, the coal burns to carbon dioxide. This, as it passes up through the column of glowing coal, changes to carbon monoxide, which finally burns again to carbon dioxide at the top of the fuel bed, where it meets more air. If the fire is not well-handled, carbon monoxide will escape up the chimney, which means great waste of fuel. In many works it is the practice to analyze the chimney gases constantly. The firemen are fined when carbon monoxide is present, and premiums are paid them when it is absent and the composition of the gases shows that good work is being done.

139. **Effect of Carbon Monoxide Upon the Body.**—Fatal accidents often occur when the gases from stoves or furnaces are allowed to enter sleeping-rooms. The explanation is that carbon monoxide is intensely poisonous, 0.5% of it being rapidly fatal and much less by prolonged inhalation. This is due to the fact that it combines with the coloring

matter (hæmoglobin) of the red blood corpuscles, forming a compound, and preventing them from doing their work of carrying oxygen about the body. Carbon monoxide poisoning is therefore a kind of suffocation and 10 c.c. of it per kilogram, reckoned on the weight of the animal, is enough to cause death. Traces in the air cause violent headaches and nervous symptoms. Being odorless, it gives no warning of its presence, and insensibility comes so quickly that it is usually impossible for the victim to reach a door or window. The poisonous action of illuminating gas is due to carbon monoxide (up to 40% in modern gas). The gas connections of a house should be carefully looked after. Small leaks can be detected by the bubbling which follows when soapy water is smeared over the suspected joint. The use of gas radiators, especially in sleeping-rooms and bath-rooms, is dangerous.

The treatment of carbon monoxide poisoning is about the same as that used in cases of apparent drowning: fresh air, oxygen if available, artificial respiration, and a physician at the earliest possible moment.

If an animal is put in air under a pressure of ten atmospheres, as much as 6% of carbon monoxide can be mixed with the air without causing any symptoms of poisoning. At the high pressure, enough oxygen to support life dissolves in the *plasma* of the blood, and the fact that the corpuscles no longer supply oxygen makes no difference.

Carbon monoxide has about the same specific gravity as air. Cold and pressure convert it into a liquid which boils at −190°.

140. Combination of Gases by Volume.—A mixture of carbon monoxide and oxygen explodes when flame or electric sparks are applied, producing carbon dioxide. Information about the volumes of the two gases which unite can be obtained (a) by calculation from the quantities by weight (b) by direct measurement.

(a) From the equation,

$$CO + O \longrightarrow CO_2$$

we note that 12 + 16, or 28, grams of carbon monoxide unite with 16 grams of oxygen, producing 44 grams of carbon dioxide. The weight of 1 liter of carbon monoxide is 1.25 grams. The volume of these 28 grams will be

$$\frac{28}{1.25} = 22.4 \text{ liters}^1.$$

---

[1] In all calculations of this kind the gases are supposed to be at the standard temperature 0° and the standard pressure of 760 m. m

Since the weight of a liter of oxygen is 1.429 grams, the volume of the 16 grams of oxygen will be

$$\frac{16}{1.429} = 11.2 \text{ liters.}$$

The weight of 1 liter of carbon dioxide is 1.965 grams and the volume of the 44 grams will be

$$\frac{44}{1.965} = 22.4 \text{ liters.} \quad \text{Therefore}$$

$$\begin{array}{c}22.4\text{ liters of}\\ \text{carbon monoxide}\end{array} + \begin{array}{c}11.2\text{ liters of}\\ \text{oxygen}\end{array} \longrightarrow \begin{array}{c}22.4\text{ liters of}\\ \text{carbon dioxide.}\end{array}$$

Dividing through by 11.2 and writing volumes instead of liters, we get

$$\begin{array}{c}2\text{ volumes of}\\ \text{carbon monoxide}\end{array} + \begin{array}{c}1\text{ volume of}\\ \text{oxygen}\end{array} \longrightarrow \begin{array}{c}2\text{ volumes of}\\ \text{carbon dioxide.}\end{array}$$

(b) Direct measurement confirms this. A *eudiometer* is a graduated glass tube (Fig. 37). In the upper part are two platinum wires, between which a spark can be passed. 20 c.c. of carbon monoxide and 10 c.c. of oxygen are allowed to enter the tube. The level of the mercury in both limbs must be made the same when the measurements are taken. Then the spark is passed. There is an explosion, and 20 c.c. of gas remain. This can be proved to be carbon dioxide by letting a little potash lye pass up into the tube. The gas is completely absorbed.

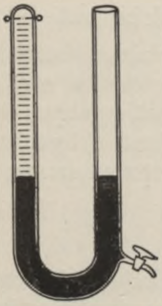


FIG. 37.—Synthesis of carbon dioxide from carbon monoxide and oxygen.

141. General Statement.—We are now ready to make a general statement about the combination of gases by volume.

(1) *When two gases combine there will be a simple relation between their volumes.*

(2) *If the compound is also a gas, there will be a simple relation between its volume and that of each of the gases which have united to form it.*

The phrase "simple relation" sometimes offers difficulties to the student. To say that there is a "simple relation" between two things means that they are equal, or that one is twice as great as the other, or that one is to the other as 2 is to 3 and so on. It means that there is a relation between them which can be expressed by small whole numbers.

The law expressed in (1) and (2) was stated by the French chemist *Gay Lussac*, in 1808. It is called the *law of combining volumes*. It applies *only to gases*. The instances we have studied thus far are these:

1 volume of oxygen + solid sulphur ⟶ 1 volume of sulphur dioxide.

2 volumes of sulphur dioxide + 1 volume of oxygen ⟶ solid sulphur trioxide.

1 volume of oxygen + solid carbon ⟶ 1 volume of carbon dioxide.

2 volumes of carbon monoxide + 1 volume of oxygen ⟶ 2 volumes of carbon dioxide.

(1) The elements combine with each other in the quantities indicated by the atomic weights, or in small multiples of those quantities. But (2) they also combine in equal volumes, or small multiples of equal volumes. Therefore (3), the atomic weights (in grams) of the gaseous elements must occupy equal volumes, or small multiples of equal volumes.

Oxygen and nitrogen are the only gaseous elements we have studied upon which we can test this conclusion. We have just noted (p. 108) that 16 grams of oxygen fill a volume of 11.2 liters. The atomic weight of nitrogen is 14 and the weight of 1 liter is 1.25 grams. Hence the volume filled by the atomic weight will be $\frac{14}{1.25} = 11.2$ liters, which is identical with the result obtained for oxygen. The same calculation for the other gaseous elements would give the same result. The volume of the atomic weight would be 11.2 liters.[1] We shall not here discuss the case of sulphur, mercury and many other elements, which exist as gases only at high temperatures.

142. Compound Gases.—Finally, a word about compound gases. Of course there are no special atomic weights for compounds. The sum of the atomic weights of the elements in the formula gives the *molecular weight* of the compound, and

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[1] This reasoning is based upon the behavior of the elements when they form compounds. It has no bearing, therefore, upon argon and the other elements which form no compounds.

this is the weight of it which enters into chemical changes. Let us repeat a few of the equations into which compounds enter

$$SO_2 + O \longrightarrow SO_3$$
$$CO + O \longrightarrow CO_2$$
$$CO_2 + Zn \longrightarrow ZnO + CO$$
$$CO_2 + C \longrightarrow 2CO$$

28 grams of carbon monoxide, 44 grams of carbon dioxide and 64 grams of sulphur dioxide are the molecular weights of those substances, the quantities in which they enter chemical changes. We have shown that 28 grams of carbon monoxide and 44 grams of carbon dioxide each fill a volume of 22.4 liters. What about the molecular weight of sulphur dioxide? One liter of the gas weighs 2.86 grams. Hence 64 grams of it will fill a volume of

$$\frac{64}{2.86} = 22.4 \text{ liters.}$$

The molecular weights of all gases fill the same volume. This volume is 22.4 liters, if the unit of weight is the gram and the pressure and temperature are standard.

To get an idea of this volume, think of a cube about the size of a cubic foot. The side of this cube is 11.1 inches (28.19 cm.). Such a cube would hold 22.4 liters. To determine the molecular weight of any gas we should only have to fill the cube at S.T.P. (**S.T.P. means standard temperature and pressure**) and find the weight of the gas in it.

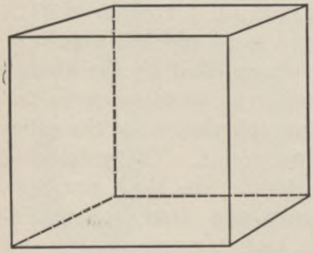

FIG. 38.—Standard cube which would hold the molecular weights of all gases, taken in milligrams.

The cube is indicated reduced to $\frac{1}{10}$ the real diameter in Fig. 38. The cube in the drawing has $\frac{1}{1000}$ the volume of the real one and holds 22.4 c.c. The molecular weights of all gases in *milligrams* (1 milligram = 0.001 gram) would, at S.T.P., fill the cube in the figure.

Since the relation between the gram and the ounce (avoirdupois) is the same as the relation between the liter and the cubic foot, it follows that the molecular weights of all gases taken in *ounces* will occupy 22.4 *cu. ft.* If we took the molecular weights in *pounds* their volume would be 22.4 × 16 = 358.4 cu. ft., but the molecular weights of the different gases would still fill the same volume. That is the essential thing, that the volumes are the *same* for different gases. The number 22.4 is merely an accident which depends upon the magnitude of the gram and the liter.

143. **Carbon Suboxide.**—*Carbon suboxide,* C_3O_2, is at low temperatures a colorless liquid with a strong irritating odor recalling that of mustard. It boils at 7°. It is combustible. When kept in a sealed glass tube, it changes to a dark red solid.

Definitions

Catalyst. A substance which increases the speed of a chemical change between other substances, but remains itself unaltered.

Catalyzer. Same as catalyst.

Catalytic action. A chemical change in which a catalyst is employed.

Contact action. Same as catalytic action.

Gravimetric analysis. Analysis by starting with a weighed sample, and weighing the products obtained from it.

Volumetric analysis. Analysis in which the results are obtained by measuring volumes of gases or liquids.

Critical temperature. The temperature above which a gas cannot be liquefied by pressure. When heated to the critical temperature, a liquid is converted into vapor, no matter what the pressure may be.

Molecular weight. The sum of the atomic weights of the symbols in the formula of a substance.

CHAPTER IX

WATER AND HYDROGEN

144. Water in Nature.—About three-fourths of the surface of our planet is covered with water. This water is in constant circulation. It is evaporated from the oceans by the sun's heat and blown over the land, on which, when condensed by cooling, it falls as rain. Upon this constant circulation, the plant life and animal life of the world depend.

Rain is the purest natural water, but even while in the air, it absorbs gases and is contaminated with dust and bacteria. When it reaches the surface of the earth, the water begins to take up mineral matter from the soil and the rocks. Sea-water contains more than 3% of dissolved matter, chiefly salt. The waters of the Dead Sea and the Great Salt Lake contain upwards of 25% of dissolved solids—so much that aquatic life does not exist in them. River and brook waters contain smaller quantities of mineral matter—usually much less than 0.1%.

Mineral waters are spring waters which contain such large quantities of dissolved material that they have a marked flavor and a special action of some kind upon the body.

145. Purification of Water for Chemical Purposes.—The impurities of natural water unfit it for laboratory uses. The method of purification depends upon the fact that the water is converted into steam at a temperature of 100°, while the mineral matter does not vaporize at all at that temperature. Hence the steam, when passed through a cold tube, condenses to form water which is practically pure. Fig. 39 is a diagram which illustrates the *principle* of the process. The water is heated in a copper vessel B and the steam passes through A and C into the spiral tube D of copper or tin, which is cooled by water circulating outside it. Pure water collects in O. The mineral impurities remain in B. Glass vessels are not used because glass is decidedly soluble in water. The process is called **distillation**. It is also used

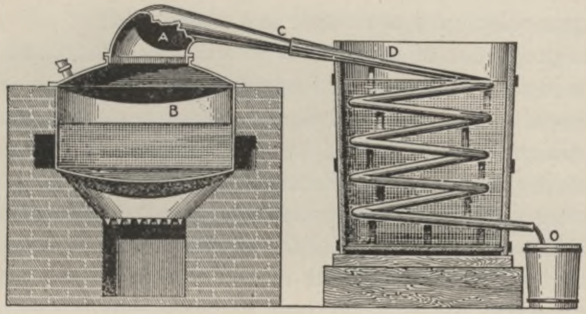

Fig. 39.—Distillation.

for purifying other liquids. The apparatus used in the laboratory, for preparing small quantities of distilled water, is shown in Fig. 40.

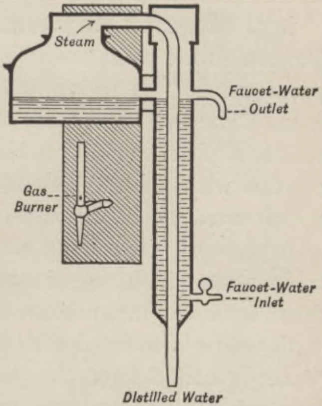

Fig. 40.—Apparatus for preparing small quantities of distilled water.

Distilled water is not *absolutely* pure. Traces of mineral matter are contained in it, and gases are absorbed from the air. In fact an "absolutely pure substance" is like the circle in mathematics, an ideal, which real things approach, but never reach. For very careful work, water is purified by several distillations, conducted with special precaution. Even then, all we can do is to reduce the impurities to such small quantities that they do not affect the behavior of the water, and can not, therefore, be detected in it.

146. Properties of Water.—Water is blue. The color is faint, but it can easily be seen when a porcelain bath-tub is filled, and in a layer two meters or more in thickness it becomes very distinct. This is one cause of the bluish color of large bodies of clear water in lakes and in the ocean. Ice has the same color, very noticeable in a glacier.

The properties of water fit it to serve as a standard substance in several important respects. Its freezing-point and boiling-point under one atmosphere pressure give us the two fixed points 0° and 100° of the centigrade scale. The corresponding points on the Fahrenheit scale are 32° and 212°. The mass of a cubic centimeter of water at the temperature at which water is densest (nearly 4°) is the unit of mass, the **gram.** The amount of heat required to warm 1 gram of water from 15° to 16° is the unit of the quantity of heat, the **calorie.** Water at 4° is the unit of specific gravity. The statement that the specific gravity of platinum, for instance, is 21.5 means that 1 c.c. of platinum weighs 21.5 times as much as 1 c.c. of water at 4°.

147. **Action of Magnesium on Water.**—When we studied air, we found that its behavior with metals at high temperatures led us to an understanding of its chemical nature. The fact that iron, zinc and other metals rust when wet is a plain indication that water enters into a chemical change with them. Let us try with water the same plan which was successful with air.

A piece of magnesium ribbon burns brilliantly in air to a white mass which weighs more than the magnesium and which must consist of magnesium oxide. A beaker one-fourth filled with water is covered with a perforated asbestos plate. The water is boiled until the steam has expelled all the air and burning magnesium is introduced. The combustion goes on with undiminished brilliancy and the substance produced has all the properties of the oxide formed by burning the metal in air. This indicates that *oxygen* is one of the constituents of water. If the experiment is made in a dark room, a pale flame can be seen, burning around the hole in the plate. Assuming that water contains two elements, one of which is oxygen, it is plain that the other must be set free when the oxygen combines with magnesium. It would seem that the other constituent is a combustible gas, which is liberated inside the beaker, and burns when it meets the oxygen of the air outside.

148. Action of Zinc and Iron on Water.—A simple way of investigating the behavior of zinc and iron with water is described in the laboratory studies. Fig. 41 shows an experiment for the lecture table. Steam is passed over hot powdered zinc or iron contained in a hard glass tube. The gas issuing from this tube is collected over water. The zinc turns to white zinc oxide, while the iron forms the same blue-black oxide (magnetite) which it yields when burned in air or oxygen. A colorless gas collects over the water. This is the other constituent of which we are in search. It is called **hydrogen.** It is easily obtained by the method described in the laboratory studies (interaction of zinc and sulphuric acid).

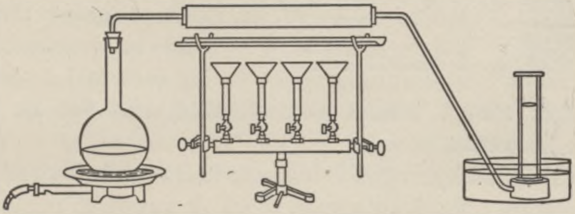

FIG. 41.—Action of heated zinc on steam.

149. Properties of Hydrogen.—When pure, hydrogen is odorless. From the fact that we have collected it over water it follows that its solubility in that liquid must be small. An experiment like that described on p. 72 shows that 100 c.c. of water at 0° dissolve only 2 c.c. of hydrogen. When a liter flask full of air is weighed, and then weighed again after the air has been displaced by hydrogen, the flask is found to be about 1.2 grams lighter than before. Hydrogen is much the lightest of gases. A liter of it at S.T.P. weighs only 0.09 gram.

150. Liquefaction of Hydrogen.—Like all other gases which are slightly soluble in water, hydrogen is hard to liquefy. Sir James Dewar liquefied the gas in 1898 by subjecting it to great pressure and cold (Chap. XIII). Liquid hydrogen is colorless and only $\frac{1}{14}$ as dense as water. It is by far the lightest of liquids. It boils at -253°. A vessel containing it becomes covered, in a little while, with a white layer of solid air. Dewar led various gases through tubes into vessels standing in liquid hydrogen. All gases except helium became solid, and fell as snow to the bottom.

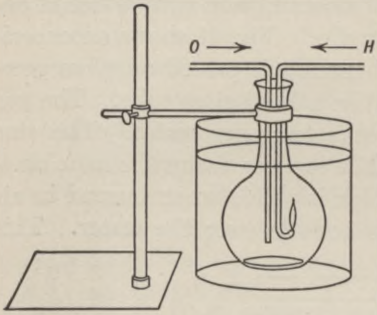

Fig. 42.—Synthesis of water.

When liquid hydrogen is made to boil rapidly by reducing the pressure upon it by means of an air pump, so much heat is absorbed that the liquid freezes to a mass resembling ice. Solid hydrogen has about the same density as the liquid and is the lightest of solids.

151. More About the Composition of Water.—Henry Cavendish, who was born in 1731 and died in London in 1810, was the first to point out that hydrogen is an element. He called it "inflammable air." He was also the first to show that, when it combines with oxygen, water is the only product. When dry hydrogen is burned under a cold inverted jar the glass is covered with fine drops of water. That this results from the combustion of the gas is shown by the fact that the deposit is not produced when the hydrogen, without being lighted, is simply allowed to escape under the jar. 20 or 30 c.c. of water can be quickly obtained by the experiment shown in Fig. 42. Hydrogen is burned in a flask immersed in water to keep it cold. Oxygen is run into the flask through a separate tube. Care is required not to allow a mixture of the two gases to form in the flask, as this would lead to an explosion.

152. Quantitative Data.—To obtain quantitative information we may choose (a) the volumetric or (b) the gravimetric method

(a) The apparatus is the eudiometer shown in Fig. 43. We fill it with mercury and invert it in a narrow cylinder containing the same liquid. Then we introduce say 10 c.c. of hydrogen and 10 c.c. of oxygen and pass the electric spark between the platinum wires. There is a slight explosion. Since the tube is cold, the water which is formed condenses to a liquid whose volume is so small that it cannot be measured on the graduations. 5 c.c. of gas remain, which the spark test shows to be *oxygen*. Thus 10 c.c. of hydrogen unite with 5 c.c. of oxygen, or

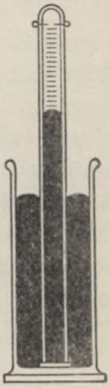

FIG 43.—Composition of water by volume.

$$2 \text{ Volumes of hydrogen} + 1 \text{ Volume of oxygen} \longrightarrow \text{water.}$$

The atomic weight of hydrogen is 1.01 and the weight of a liter at S.T.P. is 0.09 gram. The volume at S.T.P. of the atomic weight will be

$$\frac{1.01}{0.09} = 11.2 \text{ liters.}$$

We have seen that the volume of the atomic weight of oxygen (16 grams) at S.T.P. is also 11.2 liters. Therefore, at S.T.P.

$$\underset{\substack{\text{2 atomic weights}\\ \text{of } hydrogen}}{11.2 \text{ liters} \times 2} + \underset{\substack{\text{1 atomic weight}\\ \text{of } oxygen}}{11.2 \text{ liters}} \longrightarrow \text{water}$$

Therefore the simplest formula of water is H_2O.

(b) Hydrogen, at a red heat, removes the oxygen from many oxides of the metals, forming water and setting free the metal. For example:

Cupric oxide + Hydrogen → Copper + Water
Magnetite + Hydrogen → Iron + Water.

A gravimetric method for ascertaining the composition of water can be based upon this behavior. The apparatus is shown in Fig. 44. The combustion-tube contains cupric oxide. It is disconnected and weighed before and after the experiment. The absorption tubes are also weighed before and after the experiment. They are intended to collect the water formed. Most of the water condenses in the bulb and the rest is caught by the U-tube, which contains glass beads wet with strong sulphuric acid, which eagerly absorbs water. Pure dry hydrogen is led through the apparatus from left to right and the cupric oxide is heated to faint redness.

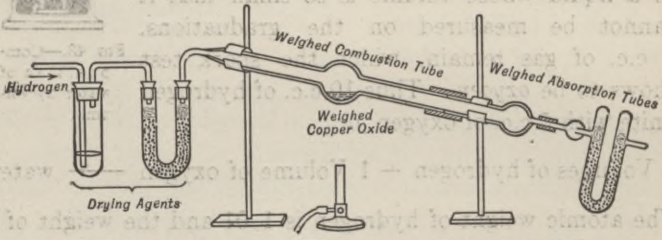

Fig. 44.—Composition of water by weight.

After the experiment, the combustion-tube contains copper, and its loss in weight is the oxygen which has combined with the hydrogen to form water. The weight of this water is obtained from the gain of the absorption tubes. Suppose that the loss in weight of the combustion-tube = 1 gram, and that the gain of the rest of the apparatus = 1 . 1263 gram. Then the hydrogen which formed water = 0 . 1263 gram, and the weight which would unite with 16 parts of oxygen is given by the proportion

$$1 : 0.1263 :: 16 : x \quad \therefore x = 2.02 \text{ grams.}$$

Since the atomic weight of hydrogen is 1.01, this means two atomic weights, and the simplest formula is H_2O.

Related Topics

153. **Iron Oxide and Hydrogen.**—When powdered *magnetite* is used in the experiment of Fig. 44, water is formed in the same way and iron is left. But we saw on page 115 that iron powder will attack steam, setting free hydrogen and forming magnetite. It seems, therefore, that the reaction

$$\text{Iron} + \text{steam} \rightleftarrows \text{magnetite} + \text{hydrogen}$$

is reversible, like the formation of silver oxide (p. 83). In this case, also, the explanation is obtained by a study of the influence of *concentration* on the progress of the change.

(1) When steam is passed over heated iron, the liberated hydrogen is swept away at once and has no chance to act upon the iron oxide which is formed. The concentration of the hydrogen is kept *low*. But the concentration of the steam is kept *high*. Hence it acts upon the iron until the metal is all converted into oxide.

(2) When hydrogen is passed over heated iron oxide, the process is reversed. The constant supply of hydrogen keeps its concentration *high*. The steam is removed as fast as produced, so that its concentration cannot rise much above zero. Scarcely any steam is offered to the iron, while hydrogen is generously offered to the iron oxide. Hence the oxide is converted into the metal.

We may build a general statement on this basis. *In a reversible change, an increase in the concentration of a substance causes the change to proceed in the direction in which that substance is consumed.* Thus, in this case, if the concentration of the steam is increased, iron oxide and hydrogen are formed, which consumes some of the steam. If the concentration of the hydrogen is increased, iron and water are formed and some of the hydrogen disappears.

154. Use of Hydrogen in Analyzing Air.—Suppose we had a measured volume of air, confined over water. If a hydrogen flame was introduced, it would go on burning till the oxygen was used up, and would then be extinguished. The water formed would condense and occupy a volume too small to measure. Therefore the shrinkage in the volume of the air would measure the quantity of oxygen.

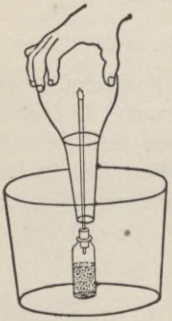

Fig. 45.—Burning hydrogen in a confined volume of air.

This method was used by Scheele. A drawing of his apparatus is given in Fig. 45. He obtained the total capacity of the flask by filling it with water and pouring the water into a graduated vessel. The water which entered during the combustion, and which was equal in volume to the oxygen which had disappeared, he measured in the same way.

It is much more exact to mix hydrogen with a measured volume of air in a eudiometer (Fig. 43). A more convenient style of eudiometer for the purpose is shown in Fig. 37. When the spark is passed there will be an explosion due to the formation of water, which at once condenses. Water is formed from two volumes of hydrogen and one volume of oxygen. Hence, one-third of the shrinkage in volume is the oxygen, which has disappeared.

Suppose that we took 16.7 c.c. of air and added enough hydrogen to make the total volume 29 c.c. After the explosion, the volume was only 18.5 c.c. The contraction was 29 — 18.5 = 10.5 c.c. One-third of 10.5, or 3.5 c.c., is the volume of the oxygen, and its percentage by volume is

$$\frac{3.5}{16.7} \times 100 = 20.95\,\%.$$

155. Combustion.—The word *combustion* has about the same meaning as the ordinary term *burning*. We have used it to apply to rapid union with oxygen, accompanied by the production of light and much heat. Oxygen is not the only gas which may support combustion. A few substances burn in nitrogen and quite a number in hydrogen. Later, we shall study active gases, like *chlorine*, in which violent combustions occur.

However, combustion in the *air* is union with oxygen. In anthracite coal and coke, it is chiefly carbon which burns. Soft coal, wood, kerosene, gasoline, illuminating gas and candles contain much hydrogen, in chemical union with carbon. When they are burned, water and carbon dioxide are produced.

From the behavior of ordinary fuels it is clear that carbon and hydrogen must produce great quantities of heat when they unite with oxygen. Exact measurement shows that one gram of carbon, when burned, produces enough heat to raise the temperature of 83 grams of water from the freezing- to the boiling-point. The corresponding number for hydrogen is 350. The burning of one gram of hydrogen to water produces more heat than can be obtained, by any other chemical process, from one gram of material.

156. Rapid and Slow Combustion.—The rusting of metals is mainly slow union with oxygen in the cold, that is, slow combustion. Carbon burns slowly in the same way, though the product is not a rust, but an invisible gas, carbon dioxide. Samples of coal are usually sent to the chemist for analysis in sealed fruit jars. In less than a week, all oxygen has vanished from the air in the jar and united with the constituents of the coal. Moissan sealed up charcoal powder with oxygen in glass tubes and kept them at 100°. After a month he cooled one end of the tube with liquid air. A snowy deposit of solid carbon dioxide (p. 101) proved that combination had taken place. A similar slow combustion occurs in the body, where the carbon and hydrogen of complex compounds unite with oxygen derived from the blood. This is the source of the heat which keeps the temperature of warm-blooded animals above that of their surroundings.

We have seen (p. 24) that copper combines slowly with sulphur in the cold and that high temperature quickens the combination until it becomes a combustion. We also found that it was sufficient to heat one portion of the mixture of copper and sulphur. The heat evolved at this point raised the temperature of the neighboring portions, and the whole mass was finally transformed to copper sulphide without any further application of heat. The combination of carbon with oxygen is similar and the accelerating effect of high temperatures supplies a complete explanation of it.

The speed of a moving body is measured by the distance it travels per second. The speed of a chemical process is measured by the *weight of material* transformed per second. Measurement shows that, on an average, the speed of a chemical change is doubled by a rise in temperature of 10°.

There is no temperature at which coal *begins* to burn. It burns very slowly in the coal bin and much more rapidly when shovelled into the furnace, because its temperature is higher by about 1000°. In order to appreciate the enormous effect that this would have upon the speed of the combination consider that:

A rise of 10° multiplies the speed by 2
A rise of 20° multiplies the speed by $2 \times 2 = 2^2$
A rise of 30° multiplies the speed by $2 \times 2 \times 2 = 2^3$
A rise of 1000° multiplies the speed by 2^{100}

2^{100} is about equal to the number 126 followed by 28 ciphers. Evidently the accelerating effect of high temperature is quite competent to explain why coal combines so much more rapidly with oxygen at a red heat.

The control of the furnace is effected, not by regulating the temperature directly—which would be complicated from a practical point of view—but by controlling the rate at which oxygen is admitted to the fuel bed. No matter what the speed of combination may become, the coal cannot combine with more oxygen than is offered to it.

The slow combustion of coal, especially of bituminous coal, is an important practical matter where thousands of tons are stored. It often happens that enough heat is developed to set fire to the mass. Even when this does not occur, the slow combination with oxygen will, in a short time, seriously reduce the heating value of the coal. Therefore large quantities of bituminous coal are best stored under water, to prevent the access of oxygen.

157. Flames.—Sulphur burns in oxygen with a large pale flame: iron burning in oxygen, gives a brighter light and a higher temperature, but no flame is seen. The cause of this striking difference is that sulphur is much more easily converted into vapor (more *volatile*) than iron. It boils at 448°, which is below a red-heat; iron only at the temperature of the electric arc. So the sulphur is vaporized by the heat of its own combustion and its vapor streams out into the surrounding space to meet the oxygen. This space becomes filled with a mixture of hot sulphur vapor, sulphur dioxide and oxygen, which makes up the flame.

Iron is not vaporized at all by the temperature produced when it combines with oxygen. The oxygen must go to the iron, and the combination takes place entirely at the surface of the metal. The iron glows brightly, but since the chemical change does not extend into the surrounding space, there is no flame.

It seems, then, that we have a basis for two general statements:

1. A solid which is not converted into vapor or gas while burning, will burn without flame. If conversion into gas or vapor takes place, a flame is formed. Since the latter case is the more common one, combustion with flame is much more frequent than without it.

2. A combustible *gas* will always burn with a flame. This proposition is really included under (1).

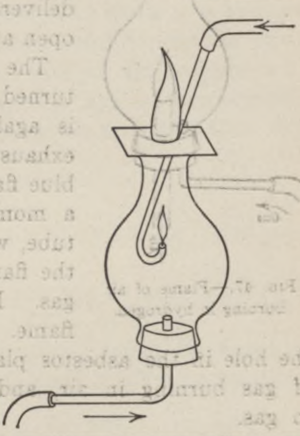

FIG. 46.—Oxygen burning in hydrogen.

The laboratory work will afford material for testing the truth of these statements.

158. Reversed Flames.—Hydrogen burns with a hot blue flame in air or oxygen. Suppose we reverse the arrangement, delivering oxygen through a tube into a vessel full of hydrogen, what would be the result? Since the same chemical change could occur, we might predict that a very similar flame would be obtained.

A lamp chimney (Fig. 46) affords an inexpensive apparatus for investigating the question. It is closed below by a rubber stopper, bearing a tube to deliver the hydrogen. Illuminating gas is cheaper and answers the same purpose. A perforated asbestos plate is laid on the top to avoid breakage, and the gas is lighted. A mouth blowpipe carrying a gentle current of oxygen from a cylinder is lowered into the chimney. The oxygen takes fire and continues burning with a pale hot flame exactly like that of burning hydrogen.

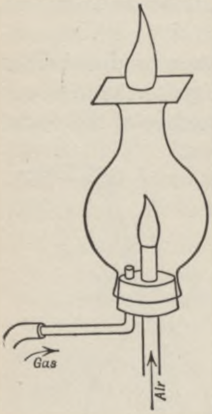

FIG. 47.—Flame of air burning in hydrogen.

By means of the apparatus of Fig. 47 a flame of air burning in illuminating gas can be obtained. The right-angled tube delivers the gas; the short wide tube is open at both ends.

The stopper is taken out, the gas turned on and lighted. When the stopper is again inserted, the gas flame soon exhausts the oxygen in the vessel; a pale blue flame floats about the chimney for a moment and then settles on the air tube, where it continues to burn. This is the flame of air, burning in illuminating gas. It looks exactly like the Bunsen flame. The gas may now be lighted at the hole in the asbestos plate and we have above the flame of gas burning in air, and below the flame of air burning in gas.

159. Evaporation.—From every-day life we can derive the following qualitative information about the evaporation of water:

1. It is rapidly converted into steam at 100°. When the water has begun to boil all the heat offered is consumed in changing the liquid to steam, so that the temperature remains at 100° until the change is complete.

2. This change,

$$\text{Water (liquid)} \rightleftarrows \text{Water (vapor)},$$

takes place slowly at lower temperatures. Countless facts, such as the drying of sprinkled roads and washed clothing, give evidence of this. The fact that wet garments can be dried out of doors in cold weather, when the moisture they contain is frozen, is a proof that water vapor escapes continually from *ice* as well as from liquid water.

3. It follows from (2) that the air must contain water vapor. The dew which forms on the outside of the ice pitcher confirms this and illustrates condensation by cooling. The frost tracery which forms on windowpanes shows that water vapor may condense to ice, without passing through the liquid stage.

Since three-fourths of the earth's surface is covered with water, we shall not be surprised at the fact that the air, on an average, is two-thirds saturated with water vapor. We should not allow the word "saturated" to lead us into the error that the air soaks up water after the manner of a cloth or a sponge. The water vapor is in exactly the same condition as the other atmospheric gases. It occupies a share of the volume and exerts a share of the pressure. Since it has a lower specific gravity than nitrogen or oxygen, damp air is *lighter* than dry air.

Definitions

Distillation. The purification of a liquid by boiling it and condensing the vapor.

Calorie. The unit of heat. The quantity of heat which will warm one gram of water from 15° to 16°.

Reversible. A term applied to a chemical change which can be driven either forward or backward by changing the concentrations of the interacting substances.

Flame. Combustion in which the burning substance is a gas, or is converted into a gas in the flame.

Evaporation. The escape of vapor from liquids below the boiling-point.

CHAPTER X

SOME IMPORTANT OXIDES FOUND IN NATURE: TIN DIOXIDE, ALUMINIUM OXIDE, MANGANESE DIOXIDE, SILICON DIOXIDE.—THERMO-CHEMISTRY

160. Tinstone.—*Tinstone* is the name given by miners to a mineral which occurs in Bolivia, in Cornwall, England, in the Malay Peninsula and some of the neighboring islands, and in the Black Hills (S. Dakota). Its color is usually brown. Often it is found without distinct crystallization, in veins, or in pebbles along the beds of streams. The latter can at once be distinguished from ordinary stones by their high specific gravity (7).

161. Composition of Tinstone.—When pure powdered tinstone is heated strongly in hydrogen in the apparatus of Fig. 44 water is formed and *tin* remains in the bulb. Tinstone is therefore an *oxide* of tin. Quantitative work shows that the atomic weight of tin (119 grams) is in combination with 32 grams (two atomic weights) of oxygen. The symbol of tin is Sn, from the Latin word *stannum*. The formula of tinstone must be SnO_2 and the chemical name, *tin dioxide*. The name *stannic oxide* is also used, to distinguish it from another oxide which has the formula SnO and is called *stannous* oxide.

162. Action of Carbon on Tinstone.—When a mixture of powdered tinstone with charcoal is heated in a hard-glass test tube with a delivery tube dipping into limewater, the latter becomes turbid. Melted tin remains in the test tube.

$$SnO_2 + C \longrightarrow CO_2 + Sn.$$

Carbon acts in the same way upon many other oxides. The removal of oxygen from an oxygen compound is called *reduction*. Tin dioxide is *reduced* by hydrogen and by carbon.

The opposite of reduction, the *addition* of oxygen to a substance, is *oxidation.*

The formula of tin dioxide can be confirmed by oxidizing a weighed quantity of pure tin foil in a porcelain crucible and weighing the tin dioxide, which is identical with powdered tinstone. 119 parts of tin combine with 32 parts of oxygen by weight.

163. **Tin.**—*Tin,* the metal of tinstone, is a silver white metal, with a brilliant luster. Its specific gravity is 7.3. It is harder than lead, but softer than gold. At ordinary temperatures it is malleable, and can be beaten into thin sheets (tin foil). Tin foil is much used for wrapping food products. At 100° tin is ductile; at 200° it is brittle and can be powdered in a mortar. It melts at 232° and boils at a white heat. At very high temperatures, tin burns with a white flame, to form tin dioxide, and melted tin slowly absorbs oxygen and gives the same product. In the cold, tin is scarcely affected by air or water.

164. **Gray Tin.**—*Gray tin* is an allotropic modification, which is formed when tin is kept at low temperatures for a long time. It has the same relation to ordinary tin that α-sulphur has to β-sulphur. Ordinary tin is stable above 20°, gray tin below.

Gray tin is a loose powder of specific gravity 5.8. It is attracted by the magnet. Tin stored in unheated buildings in winter sometimes turns to gray tin and crumbles. The tin organ pipes of churches are sometimes damaged in this way. Fortunately, the change of ordinary to gray tin is very slow. If it was rapid, objects made of tin would fall to pieces as soon as the temperature fell below 20°. Gray tin can be quickly converted into ordinary tin by the action of heat, for instance by pouring warm water over it.

165. **Tin Plate.**—Tin plate is made by coating sheets of soft steel with tin. The steel is cleaned and freed from rust, and then dipped into melted tin. It is very difficult to produce a really continuous coating, free from little perfora-

tions. Some important alloys of tin are mentioned in the table on p. 35.

166. Action of Tin upon the Body.—Tin compounds are very poisonous to plants, but much less so to animals. Large doses produce acute disturbances of digestion, which pass away without permanent injury. Doses of a centigram a day for eighteen months have been administered to cats, without any bad effect.

167. Production.—More than 100,000 tons of tin are produced each year, of which the Malay Peninsula and the neighboring islands furnish three-fourths; most of the remainder comes from Bolivia. Extensive deposits of tinstone exist in South Africa. Little tin is obtained in the United States.

168. Corundum.—The ruby and the sapphire are forms of a mineral called *corundum*, colored red in the first case and blue in the second by traces of impurities. The best rubies come from Burma, near Mandalay, while sapphires are found in various localities, for instance, near Helena, Montana. Both gems are made artificially. Corundum is rather common in the United States, especially in the South. *Emery* is an impure form of it, colored black by magnetite. Most of the uses of corundum depend upon its hardness. Among minerals, it comes next to the diamond in this respect. It is largely used as an abrasive for polishing and grinding.

169. Composition of Corundum.—Corundum is the oxide of a metal called *aluminium*. The oxygen and the metal are firmly united and there is no convenient way of separating them in the laboratory. It is easy, however, to prepare artificial corundum by synthesis. The powdered aluminium used for painting mail boxes forms a suitable material. A heap of it is placed upon a piece of asbestos board, which is laid upon an iron plate. The combustion is started with the burner-flame. The metal burns with an intense white light. The asbestos is usually perforated by the heat. A very high temperature (3000° or over) is attained, partly because the product of combustion is a solid and does not carry off any of the heat. A white powder of **aluminium oxide** is obtained, identical in composition with pure corundum. A quantitative experiment shows that its formula is Al_2O_3.

170. **Aluminium.**—Aluminium is a grayish white lustrous metal, which will take a high polish. In the cold it is almost unaffected by the air. It has about the same specific gravity (2.6) as glass, and is much lighter, therefore, than the other familiar metals. It melts readily (660°). No satisfactory solder for it has been found and pieces are united by welding.

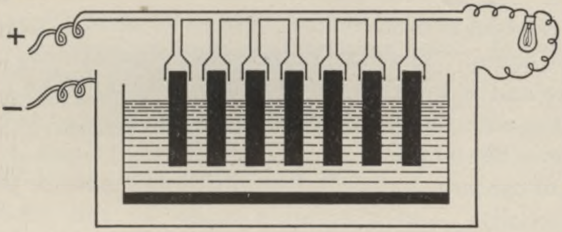

FIG. 48.—Manufacture of aluminium.

171. **Manufacture of Aluminium.**—About 25,000 tons of aluminium are made each year, and the production is increasing rapidly. The manufacture rests upon the fact that aluminium oxide, when dissolved in a suitable liquid, is decomposed by the electric current, the aluminium separating at the negative pole, the oxygen at the positive.

The liquid which has been found best for this purpose is the melted mineral *cryolite*. Cryolite is found abundantly in Greenland. It melts readily and dissolves aluminium oxide freely. The melted cryolite is contained in the rectangular box shown in Fig. 48 which is about 5 ft. long, 3 ft. wide and 6 in. deep. The box is lined with carbon and is connected with the negative pole of the dynamo. The carbon rods shown in the figure form the positive pole. They are connected with the box by a circuit in which is an incandescent lamp (shunt), so that the current can pass either through the lamp or through the liquid in the box.

When there is plenty of aluminium oxide in the bath, the current passes mainly through the liquid because it offers less resistance than does the lamp. But when the aluminium oxide is nearly all decomposed, the resistance of the bath rises and the current finds an easier way through the lamp, which lights up. Then the workman in charge shovels more aluminium oxide into the bath, which is covered with a layer of powdered coal to protect the eyes from the strong light of the red-hot liquid. The aluminium collects beneath the melted cryolite and is withdrawn from time to time. The oxygen combines with the carbon of the rods and escapes as carbon dioxide. The cryolite remains unaltered. Great care is taken to use pure materials, for aluminium cannot be purified commercially. The aluminium oxide for this process is prepared from *bauxite,* a mineral which contains chiefly aluminium oxide and water. Bauxite occurs in France and in the southern United States.

172. Uses of Aluminium: Occurrence.—On account of its lightness and strength, aluminium is used in making cameras, opera glasses, drinking cups and soldiers' canteens. It finds application in automobile construction. The pure metal makes excellent cooking utensils. These must not be cleaned with soda or ammonia, both of which dissolve aluminium. Aluminium foil is cheaper than tin foil and may be used, instead of the latter, for wrapping food products. The powdered metal, mixed with oil, is applied as a paint to metallic surfaces. Small quantities of aluminium, less than 0.1%, added to melted steel just before it is cast, cause the formation of dense, strong castings free from blowholes. Cables and wires of aluminium are used to conduct the electric current.

Aluminium bronze contains 5 to 12% of aluminium, the rest being copper. It has about the color and luster of gold and is very strong. An alloy of aluminium with small quantities of magnesium is called *magnalium*. It is used for the scales on instruments and for the beams of balances. These alloys are more easily worked than pure aluminium, which sticks to the tools.

Aluminium does not occur in the free state, but its compounds, clay and felspar for example, are among the most common minerals. In point of abundance, it is third among the elements, making up nearly 8% of the earth's crust.

173. **Historical.**—Prior to 1827, chemists had suspected for years that corundum was the oxide of an unknown metal. In that year Wöhler confirmed this suspicion by preparing aluminium. About 1850 Sainte Claire-Deville obtained it in larger quantities and, at the Paris Exposition, exhibited a bar of it labeled "L'argent de l'argile"—the silver from clay. The electric process just described is the work of an American chemist, Hall. It has reduced the price of the metal from $90 a pound (1856) to about 20 cents at present.

174. **Pyrolusite.**—*Pyrolusite* is a black mineral, soft enough to soil the fingers. It conducts the electric current and is used as the material of the positive pole of one type of cell, the negative pole being a rod of zinc and the liquid a solution of sal-ammoniac. Such cells are used for ringing door-bells and, very largely, for producing sparks in gas and gasoline engines.

175. **Composition.**—Powdered pyrolusite is mixed with granulated aluminium in a crucible, which is best lined with magnesia. The crucible is set in a bed of sand and the mixture heated at one point by burning a piece of magnesium ribbon which has been thrust into it.[1]

A chemical change starts at the heated portion and spreads through the mass, which becomes intensely hot (3000°). When the crucible is cold, it contains two substances. The upper layer is glassy and is easily identified as aluminium oxide by its extreme hardness. The lower is the metal of pyrolusite, *manganese*. Pyrolusite is *manganese dioxide,*

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[1] This heating is best done by means of a cartridge supplied for the purpose.

MnO_2, and the aluminium has taken the oxygen from the manganese.

$$3MnO_2 + 4Al \longrightarrow 2Al_2O_3 + 3Mn.$$

176. Manganese.—*Manganese*[1] is a hard, brittle, gray metal whose luster is tinged with red. Its specific gravity is 8 and it melts above a white heat (1900°). It rusts in moist air, and when the powdered metal is boiled with water, hydrogen is set free, the manganese combining with the oxygen. Compounds of the metal are widely distributed in nature, being present in many minerals. Traces are found in most soils and in the woody portions of some plants. Tobacco, coffee and tea do not grow well unless manganese is present in the soil. Sea-water contains it, and great areas of the deep sea floor are covered with round masses of pyrolusite.

177. Uses.—Manganese is used only in the form of alloys. Its alloy with copper and zinc is *manganese bronze*, which is very hard and strong. *Manganese steel* contains about 14% of manganese. It was the pioneer of the *special steels*, which have become so important of late years. Its toughness and strength make it valuable for the jaws of stone-crushers and for other objects which have to stand rough usage.

Since all iron ores contain manganese, the pig iron made from them also contains it (up to 4%). *Spiegeleisen* is pig iron containing 15–20% of manganese. The name, which means mirror-iron, is due to the brilliant facets of the crystals, which appear in the broken surfaces when a bar is fractured. In *ferro-manganese* the manganese runs up to 80%, the balance being chiefly iron and carbon. Both these alloys are widely used in steel making.

Manganese ores (pyrolusite and other oxides) are used in great quantities in the manufacture of spiegeleisen and ferro-

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[1] The similarity of the name of manganese to that of *magnesium* often leads to confusion. The two are different elements, having little resemblance to each other.

manganese. The most productive mines are in Brazil, India and the Caucasus. Russia is the chief producer.

178. Quartz.—*Quartz* is the most common of minerals. Twelve per cent of the earth's crust consists of it. Many of the most abundant rocks, like granite, gneiss, mica schist and sandstone contain it.

The shape of a typical quartz crystal is shown in Fig. 49. A hexagonal prism is terminated at each end by a hexagonal pyramid. Natural crystals have usually grown fast to the rock at one end, which is therefore not developed. Often they are found in groups.

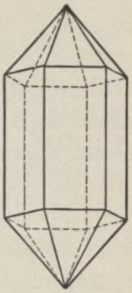


FIG. 49.—A quartz crystal.

Clear colorless quartz is called *rock crystal.* During the middle ages it was supposed to be composed of water, which had been so thoroughly frozen by intense cold, that it was impossible to melt it. When cut and polished, rock crystal makes the *rhinestone* or *quartz diamond.* It can be distinguished at once from the true diamond by its different luster and inferior hardness. Clear quartz crystal, colored violet by a little manganese is the *amethyst;* colored yellow the *false topaz.*

Quartz is also found in irregular masses composed of microscopic crystals. It is then called *chalcedony*, *agate*, *carnelian* or *onyx* according to the color and other properties. *Petrified wood* is produced when wood decays under water containing dissolved quartz. The quartz replaces decaying wood bit by bit, so that the structure of the wood is preserved. *Flint* is massive quartz which when struck with a hammer, usually breaks into pieces with a sharp cutting edge. It was used for knives and arrowheads by prehistoric man. Quartz is the chief constituent of most ordinary *sand.* Pure quartz in the form of clean, white sand, or of rock crystal, is used in great quantities in the manufacture of *glass.*

179. Opal.—*Opal* has nearly the same composition as quartz, but is amorphous. It is also less pure, containing water and usually ferric oxide as impurities. *Infusorial earth* is a mass of minute shells consisting of opal. It is used in scouring powders and for the manufacture of dynamite. When opal exhibits a beautiful play of colors, it is used as a gem. The finest stones come from Hungary, Mexico, Australia and Honduras.

180. Silicon.—Quartz is an oxide and, when the powdered mineral is heated with magnesium, there is a violent reaction which may be explosive. The oxygen of the quartz combines with the magnesium and the other element is obtained as a brown powder. It is called **silicon.** Quartz is *silicon dioxide*, SiO_2, and the equation is

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO.$$

Sand consists chiefly of rounded grains of quartz, and silicon is now made on a large scale by heating a mixture of sand with coke to the high temperature of the electric furnace.

$$SiO_2 + 2C \longrightarrow Si + 2CO.$$

Silicon made in this way is a gray, lustrous crystalline mass, harder than glass and nearly three times as dense as water. Its chief use is in the manufacture of steel. Small quantities of silicon added to the melted metal, just before pouring into the mould, cause the formation of dense, sound ingots. We have noted the use of aluminium for the same purpose (p. 130).

181. Silicon Monoxide.—When sand is heated in an electric furnace with an amount of coke only sufficient to remove half the oxygen, *silicon monoxide*, SiO, is obtained. This is a light yellowish brown powder which bears the commercial name of *monox*. It is used as a paint.

182. Silicon Carbide, SiC.—On the other hand, when more coke is used than is needed to remove all the oxygen from the sand, the liberated silicon unites at once with carbon and forms silicon carbide, SiC, which is called *carborundum.* In practice some salt is added to the mixture of coke and sand to make it melt more readily, and some sawdust to make it porous. The reaction, however, is entirely between the sand and the carbon.

$$SiO_2 + 3C \longrightarrow SiC + 2CO.$$

The materials are contained in a rectangular furnace whose sides are built of loosely piled bricks (Fig. 50). The carbon electrodes project into the mass through the end walls. There is a core of granulated coke imbedded in the mixture, reaching from one electrode to the other. This, being a bad conductor, is intensely heated when the current is turned on. A powerful current passes for eight hours, during which time, the heat from the coke core penetrates the mass and the change indicated in the equation above occurs. The current acts only as a source of heat. The furnace is then allowed to cool and the side walls torn down to remove the product.

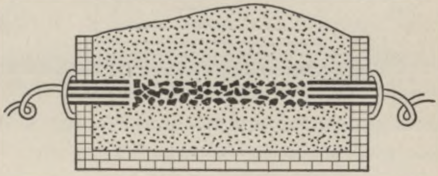


FIG. 50.—Carborundum furnace.

Carborundum when pure is in colorless crystals, but usually it is brown or black. It is harder than ruby and almost as hard as the diamond. It finds wide application as a substitute for emery in making hones, whetstones, grinding wheels and polishing paper. It is also used for the crown, or cutting edge, of rock drills.

The intense heat of the carborundum furnace converts the coke of the core into artificial graphite (p. 43).

In the manufacture of carborundum the electric current serves merely as a *heating* agent. A process of this kind in which the current is used simply as a means of obtaining a high temperature is called an *electrothermal* process. In the carborundum furnace, Fig. 50, the high temperature is produced by the passage of a heavy current through a bad conductor against a high resistance. Fig. 50 will serve as an example of the *resistance type* of electric furnace, in which an elevated temperature is produced by putting a badly conducting body of some kind into the path of the current. We have seen that such furnaces are in extensive use.

The *arc type* of electric furnace is shown in Fig. 51. The arc is made to burn between heavy carbon rods below which is placed the crucible containing the substance to be heated. The crucible and the furnace-lining must be made of some substance which is exceedingly *refractory* (difficult to melt). Furnaces in which the high temperature of the arc (nearly 4000°) is utilized are coming into wide use in the steel industry.

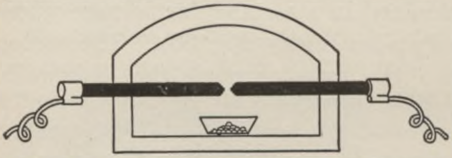


Fig. 51.—Diagram of furnace heated by an electric arc.

183. Silicon in Nature.—Although silicon does not occur in the free state, its compounds are so common that it comes next to oxygen in point of abundance, making up 28% of the earth's crust. Feldspar, mica, hornblende, and most of the other rock-forming minerals, contain it. Limestone is the only common rock which is not made up of silicon compounds. It plays, in the mineral world, somewhat the same part that carbon does in organic nature. All river, well and spring waters contain small quantities of dissolved silicon compounds.

Silicon dioxide is called *silica*. It is now made into crucibles, dishes and thermometers for the laboratory. Such ware is made by melting pure quartz with a flame of illuminating gas fed with oxygen. It is expensive, but has the merit of never cracking when suddenly heated or cooled. The stems of many plants, like rye, wheat, grass and bamboo, are rich in silica. It is also contained in sponges and in the quills of feathers.

184. Thermite.—We have noted the preparation of manganese from a mixture of manganese dioxide and aluminium. When a mixture of *ferric oxide* with one-third of its weight of granulated aluminium is strongly heated at one point, the reaction

$$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$$

begins at the heated portion and spreads through the mass, which is carried to a temperature of 3000°.

The mixture is sold under the name of *thermite*. It is useful, not for the manufacture of iron, which can be made far more cheaply by other methods, but for the production of high temperatures. Trolley rails and iron pipes are welded by means of it and broken shafts on steamships are repaired without removal.

185. Chemical Energy.—Energy, especially in the form of heat, is usually produced during chemical changes. The use made of thermite shows that, in that instance, this energy is much more important, from a purely practical standpoint, than the material products of the reaction. This is very often the case. Many chemical changes are carried out entirely for the yield of energy, the substances produced being discarded. The use of fuel is a striking example. We burn coal, wood, oil or candles to get energy as light or heat and the substances (carbon dioxide and water) which are formed at the same time are simply allowed to escape. Explosives are employed purely for the energy which they yield. Magnesium powder is burned in photographic flash-lights solely for the light energy, and the magnesium oxide produced is merely a nuisance. In the electric batteries which run our door-bells, telegraph instruments and explosion engines, we consume zinc purely to produce electrical energy, and the zinc compounds which result are discarded.

186. The Measurement of Energy as Heat.—Chemical energy is measured in the form of *heat*. The reason for this is that it is easy to carry out a chemical change in such a way that all the energy which is given out takes the form of heat, while it is impossible to obtain *all* of it in any other form. The unit of heat energy is the amount required to warm one gram of water through one degree centigrade. Practically, therefore, we carry out the chemical process, whose energy is to be measured, in a vessel which is immersed in a second larger vessel containing a known weight of water. From the rise in temperature of the water in the outer vessel, the energy yield of the chemical change which has occurred in the inner vessel is determined.

Thus, when cuprous sulphide is formed from copper and sulphur, much heat is evolved. The quantitative statement is

$$2Cu + S \longrightarrow Cu_2S + 20{,}000 \text{ calories.}$$

This means that, when two atomic weights (127 grams) of copper unite with one atomic weight (32 grams) of sulphur, enough heat is produced to raise the temperature of 20,000 grams of water 1°C. This is nearly the same as the heat required to raise 200 grams of water from the freezing- to the boiling-point. 20,000 calories is the *heat of formation* of cuprous sulphide; that is, it is the heat given out when a molecular weight of it (159 grams) is formed from 127 grams of copper and 32 grams of sulphur.

In order to break up a molecular weight (159 grams) of cuprous sulphide into copper and sulphur, *the* 20,000 *calories which escaped when it was formed must be supplied.* For otherwise we could create out of nothing any desired amount of energy by simply combining copper and sulphur (obtaining 20,000 calories) and then separating the cuprous sulphide.

187. Thermochemical Equations.—An expression like that given above, which takes account of the energy side, as well as the matter-side, of a chemical change, is called a **thermochemical equation.** Here are some additional examples:

$$\begin{array}{llllll}
(1) & C & + O_2 & \longrightarrow CO_2 & + 100{,}000 \text{ cal.} \\
(2) & H_2 & + O & \longrightarrow H_2O & + \ 70{,}000 \text{ cal.} \\
(3) & 2Al & + 3O & \longrightarrow Al_2O_3 & + 380{,}000 \text{ cal.} \\
(4) & 2Fe & + 3O & \longrightarrow Fe_2O_3 & + 196{,}000 \text{ cal.}
\end{array}$$

The large amounts of heat produced when carbon and hydrogen unite with oxygen (1 and 2) explain the universal use of substances containing these two elements for fuel. The enormous heat of formation of aluminium oxide (3) accounts for the uses of thermite. But only about half of the 380,000 cal. is available when thermite is used. The equation

$$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$$

shows that ferric oxide is separated at the same time that aluminium oxide is formed, and the 196,000 cal. required for this must be subtracted to get the actual amount of heat produced, which is

$$380{,}000 - 196{,}000 = 184{,}000 \text{ cal.}$$

for each molecular weight of aluminium oxide formed (102 grams).

An **exothermic** chemical change is one which *produces* heat. The formation of the four oxides just mentioned will serve as examples.

We have seen that, in decomposing mercuric oxide into its elements, a continuous supply of heat is required. The thermochemical equation explains this fact:

$$HgO \longrightarrow Hg + O - 21{,}500 \text{ cal.}$$

An **endothermic** change is one, which, like the decomposition of mercuric oxide, *absorbs* heat.

Definitions

Reduction. The removal of oxygen from an oxide.

Oxidation. The addition of oxygen to a substance.

Stable. Showing little tendency to change. Thus, water is a stable compound. Nitroglycerine is unstable.

Heat of formation. The heat given out when a molecular weight, in grams, of a compound is formed from its elements.

CHAPTER XI

THE ACTION OF OXYGEN ON SULPHIDES AND OF CARBON ON OXIDES.—METALLURGY OF ZINC, LEAD, MERCURY, TIN AND IRON.—WATER GAS

188. The "Roasting" of Sulphides.—The great quantities of *sulphur dioxide* which are needed for the manufacture of sulphuric acid are made from pyrite. When the mineral is heated in a current of air, it burns with a blue flame: sulphur dioxide escapes and ferric oxide remains.

$$2FeS_2 + 11O \longrightarrow Fe_2O_3 + 4SO_2.$$

The sulphides of the other common metals behave in the same way; sulphur dioxide escapes and the oxide of the metal is left.

$$(1)\ ZnS + 3O \longrightarrow ZnO + SO_2$$
$$(2)\ PbS + 3O \longrightarrow PbO + SO_2$$

The first stage in the extraction of *zinc* from *zinc blende* is to convert the sulphide into zinc oxide in this way (1). The process is called "roasting." It can be carried out in a reverberatory furnace (Fig. 52). The fuel burns at one end and the combustion products traverse the whole length of the furnace before they escape from the flue at the other. The roof is low, so that the heat is reflected down upon the charge, which is placed upon the bed of the furnace.

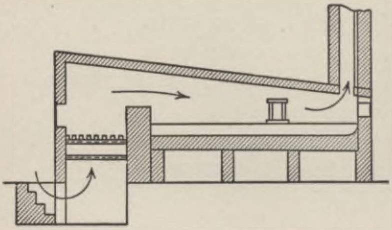


FIG. 52.—A reverberatory furnace.

In order to extract the *lead* from *lead-glance*, it is first roasted to oxide in a reverberatory furnace. About 10% of lime is mixed with the lead-glance. In some way, at present unexplained, the lime greatly facilitates the change of the lead sulphide into lead oxide. In order to avoid melting the ore, or vaporizing the lead oxide, the temperature is carefully regulated. The lead oxide, like the zinc oxide, is afterward heated with carbon (coke or coal) to obtain the metal.

189. Roasting of Cinnabar.—When cinnabar is roasted, sulphur dioxide escapes, but mercuric oxide cannot be formed, because it is decomposed by heat. Therefore the chemical change takes the course indicated by the equation

$$HgS + O_2 \longrightarrow Hg + SO_2.$$

The mercury is swept along as vapor in the stream of furnace gases and its condensation is the chief difficulty.

Fig. 53 is a diagram of the furnace and a portion of the condensing apparatus. The rectangular shaft *A* is surrounded by an iron jacket and built upon an iron plate to prevent leakage of mercury. The mixture of lumps of ore with charcoal is placed in the cup-shaped space at the top, and when the cone is lowered, the mixture slides into the furnace. A lid *c*, which is like an inverted basin with its edges dipping into water, prevents the escape of mercury vapor. Through *d*, the fire gases carrying the mercury vapor are led through condensing arrangement, which consists of a number of ∩-shaped earthenware pipes. These pipes open at the bottom into a covered cement trough, partly full of water, in which the mercury collects. The gases then pass through long underground wooden passages and stone chambers to complete the condensation.

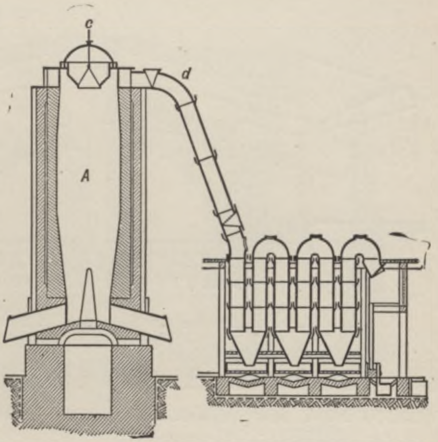


Fig. 53.—Furnace for roasting cinnabar in a current of air.

In spite of all this care, about $\frac{1}{10}$ of the mercury in the ore is lost, and the workmen suffer from mercurial poisoning.

190. Action of Carbon on Oxides.—The *oxides* which occur native, like those of tin and iron, as well as those that are made from the sulphides, like zinc oxide and lead oxide, are converted into metal by heating them with carbon (charcoal, coal or coke).

Tin oxide is mixed with anthracite coal and heated on the bed of a reverberatory furnace (Fig. 52).

$$SnO_2 + C \longrightarrow Sn + CO_2.$$

The tin is tapped off through a hole not shown in the diagram.

Lead oxide, mixed with coke, is charged in at the top of a small cylindrical blast furnace often 6 meters high and 1 meter in diameter. Through tubes which project into the furnace near the bottom a blast is introduced. The equation is

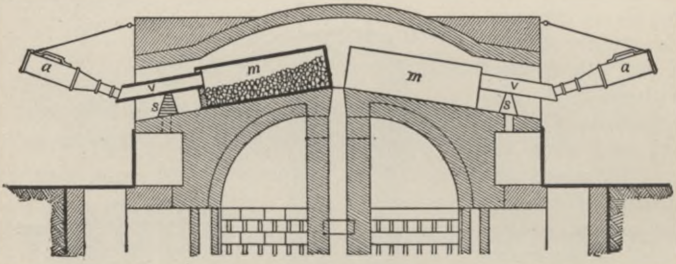


FIG. 54.—Furnace for the reduction of zinc oxide with carbon.

$$2PbO + C \longrightarrow 2Pb + CO_2.$$

The lead is tapped off below from time to time.

Zinc oxide, mixed with coke, is placed in a retort, ⌓-shaped in cross section, often 2 m. long and 50 cm. high (*m*, Fig. 54). These retorts are heated from the outside; the fuel which does the heating is separate from that which causes the reduction of the zinc oxide.

$$ZnO + C \longrightarrow Zn + CO.$$

V is a fire-clay receiver in which most of the zinc condenses. In the sheet-iron tube *a*, some of the zinc, which escapes condensation in *V*, collects as a gray powder called zinc dust, which goes back into the retort *m* with the next charge.

The first portions of this zinc dust which collect contain the *cadmium* which is often present as an impurity in zinc blende. Cadmium is a tough, soft, white metal, denser than zinc, which it resembles in chemical properties. It is used in the manufacture of fusible alloys. *Cadmium oxide*, CdO, is a brown powder. The *sulphide*, CdS, is employed as a paint under the name "cadmium yellow."

Related Topics

191. Metallurgy of Iron.—The most important ores of *iron* are oxides of the metal. Their reduction is carried out in a large round blast furnace (Fig. 55), 80–100 ft. high and 20–25 ft. in diameter at the widest part, which is below the middle. Such a furnace will produce up to 2500 tons of iron a week, consuming about an equal weight of coke and about three times the quantity of iron ore. It is built of fire brick, strengthened by iron bands.

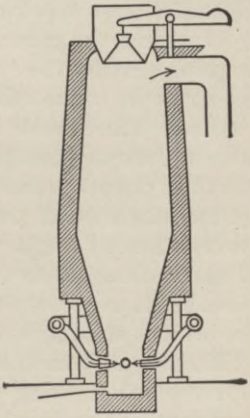


FIG. 55.—Blast furnace for the reduction of iron ore.

The blast enters through 8–10 nozzles, called *tuyères*, which are set around the furnace near the bottom. The tuyères are made double and are cooled by water circulating in the interior, for the blast has a temperature of 800° (dark red heat). The coke burns at first to carbon dioxide, which is at once converted into carbon monoxide by the glowing fuel through which it rises on its way to the top of the furnace:

$$CO_2 + C \longrightarrow 2CO.$$

The carbon monoxide removes the oxygen from the iron ore:

$$Fe_2O_3 + 3CO \rightleftarrows 2Fe + 3CO_2.$$

This reaction, as the arrows indicate, is *reversible*. In order to drive it from left to right, reducing iron oxide, the concentration of the carbon monoxide must be at least twice as great as that of the carbon dioxide. The important practical result of this is that no further reduction of iron oxide takes place in the blast furnace after the carbon monoxide in the gases is so far consumed that its percentage by volume has dropped to about twenty, the carbon dioxide at the same time having risen to about ten per cent. Even if the gases were forced through a second column of glowing iron oxide in another furnace, there would be no effect. *Equilibrium* has been reached.

Before this was understood, it was thought that the reason the gases still contained so much carbon monoxide, after passing through the furnace, was that the column of iron ore was not long enough to extract all the carbon monoxide and expensive attempts to utilize the fuel more completely by building higher furnaces were made, entirely without success.

At present, the gases are led from the top of the furnace, by a large pipe called the "down-comer," to the blast stove. This is a structure of fire brick and iron, about half the height of the furnace. The interior is of fire brick, arranged so as to offer a large surface to gases passing through it. In this arrangement the 20 % of carbon monoxide which the gas contains is burned by the admission of air and the fire brick interior of the blast stove is heated bright red. Then the direction of the current of gas is changed, so that the *air* goes through the hot blast stove on its way to the tuyères, and by contact with the red-hot fire brick is strongly heated before it enters the furnace. Meanwhile, the gas from the "down-comer" goes into another blast stove, which is being heated. To provide for cleaning and repairs, three or four blast stoves are needed for each furnace.

192. Slag.—The reduced iron in the upper part of the furnace is finely divided. As it sinks into the hot zone near the tuyères, it melts, and the liquid collects in the bottom, from which it is removed by tapping every four hours. The tap hole is then closed with moist clay which immediately bakes into a hard plug. Above this tap hole, is the *slag hole*, through which the slag is allowed to flow into tubs, which, when full, are taken to the dump. This slag is a glassy substance, which is liquid at the temperature of the furnace. It is composed of the clayey impurities of the ore (silica and aluminium oxide) together with the lime of limestone, which is added systematically with the charge through the cup and cone at the top, to assist slag formation. One important function of the slag is to cover up the liquid iron, so that it shall not be burned into oxide by the blast from the tuyères.

About a ton of slag is formed for each ton of iron. Some of it is used for road mending, roofing material and considerable quantities for cement, but the utilization of the enormous amounts which are produced is an unsolved problem.

193. Cast Iron.—Sometimes the liquid iron is run into depressions in a bed of sand in front of the blast furnace, where it freezes to bars of crude iron called *pigs*. *Cast iron* is brittle and cannot be welded or forged. Ranges, stoves, pipes, radiators and all the objects which are *cast* in ordinary foundry work are made of it. It is unsuitable for anything which is to be exposed to shock or great strain.

Cast iron is the most impure variety. It contains:

(1) *Carbon* (3 to 4%) derived from the coke.

(2) *Silicon* (up to 2%) derived from the silica of the ore.

(3) *Manganese*, a variable quantity, depending upon the ore. By using pyrolusite along with the iron ore in the blast furnace, the manganese in the pig can be run up to 20% (spiegeleisen) or even to 80% (ferromanganese). The wide use of these alloys in making steel depends upon the fact that they are rich, not only in manganese, but also in carbon.

(4) *Sulphur*, derived from the ore and the coke. This is a harmful impurity in both iron and steel, making them brittle when hot ("red short"). 0.1% makes a steel rail roll badly and very much smaller quantities are objectionable in the better grade steels which are used for railway bridges, boiler plates, ship armor, etc.

(5) *Phosphorus*, familiar from its use in making matches. It makes iron and steel brittle when cold ("cold short"). 0.1% would be rather dangerous in a rail and 0.025% is enough to spoil cutlery steel. In cast iron, its bad effect is less marked.

194. Wrought Iron.—*Wrought iron* is the purest commercial form of the metal. It is made by melting pig iron in a reverberatory furnace (Fig. 52) in contact with a layer of iron oxide. The five elements just mentioned combine with the oxygen of the iron oxide. Carbon dioxide and sulphur dioxide escape as gases; the oxides of silicon, manganese and phosphorus enter the slag. When the metal is nearly pure, it becomes semi-solid. It is then formed into balls about 80 lbs. each in weight, which are placed under a steam hammer to squeeze out the slag, and then rolled into bars. The whole operation takes about an hour and a half. The carbon can be reduced from say 4% to 0.1%; the other impurities are almost completely removed.

Wrought iron melts at a much higher temperature than cast iron. It is much tougher and can be forged and welded. It is used for nails, chains, bolts, wire, horseshoes and similar objects.

195. Steel.—Cast iron contains an average of 4% of carbon, wrought iron very little (about 0.1%). Steel is intermediate. Razor and file steel contain about 1.5%, tool-steel 1.25%, while 0.75% of carbon or less gives a soft, "mild" steel which will not hold a cutting edge. Evidently, if cast iron and wrought iron were melted together, the product would be steel, for the percentage of carbon would have an intermediate value. **Crucible steel,** which is the highest grade of steel, is still largely made by melting pure cast iron with wrought iron, or wrought iron with charcoal, in crucibles made of a mixture of graphite and fire-clay. A little ferro-manganese is added towards the end of the process. This causes the steel to be free from blowholes. The crucibles last only for three heats, and are being rapidly displaced by electric furnaces.

Crucible steel is expensive, and is used only for small objects in which quality is the first consideration. Watch springs, needles, pens, tools, razors and other cutlery are made of it.

196. Temper.—When crucible steel is heated red-hot, and then quenched in water, it becomes as hard as glass. If then re-heated, and allowed to cool slowly, it is softened to an extent depending upon the temperature of the second heating. This is called "drawing the temper." Thus if re-heated to 230°, the steel is still very hard and is suitable for razors and surgical instruments. Re-heating to 270° gives a somewhat softer, less brittle steel, useful for axe heads. The importance of this process, in fitting the steel for various purposes, is plain.

197. Bessemer Steel.—The great quantities of cheap steel used for girders, highway bridges and rails are, in part, made by the *Bessemer process.* Melted cast iron is taken from the blast furnace in a great ladle and poured into the *converter* (Fig. 56), which is a pear-shaped vessel, often 15 ft. high by 8 ft. in diameter, made of steel, lined with bricks rich in silica (SiO_2). Here a blast is forced through the liquid metal from fire clay tuyères in the bottom. The silicon and manganese are oxidized first and pass into the slag. Then the carbon oxidizes, and escapes as carbon monoxide, which burns to carbon dioxide with a bright flame at the mouth of the converter. The sulphur and phosphorus are not affected. When the removal of the carbon is complete, enough melted spiegeleisen is added to put the desired quantity of carbon and manganese into the steel, which is then cast.

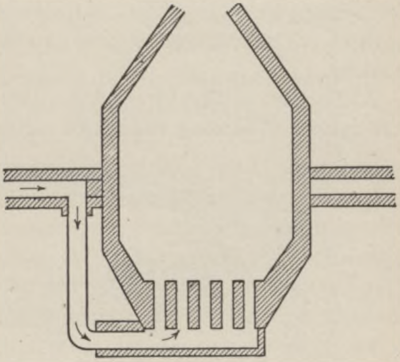


FIG. 56.—Converter.

Since phosphorus is not removed in the ordinary Bessemer process, it is necessary to use iron almost free from this undesirable element. If, however, the converter is lined with a mixture of magnesium oxide and lime, the phosphorus unites with these materials, leaves the metal and passes into the slag. Good steel can thus be made from iron rich in phosphorus. This important modification is called the *Basic Bessemer process.* It is largely used in Europe, but not in this country, because the ores are not suitable. On account of the phosphorus which it contains, the slag of the basic process forms a valuable fertilizer.

198. Open Hearth Steel.—The *open hearth process*, by which large and increasing quantities of steel are being made, is, from a chemical point of view, similar to the manufacture of wrought iron (p. 146). Melted iron is taken from the blast furnace to the hearth of a great reverberatory furnace, where it is heated with iron oxide (iron ore) until most of the carbon, silicon, manganese, phosphorus and sulphur are removed by oxidation. This requires twelve hours or more. Then enough spiegel or ferro-manganese is added to introduce the desired amount of carbon. The manganese prevents blowholes and gives a sound casting.

A diagram of the furnace is given in Fig. 57. The *regenerative system of heating* should be noted. The gas, which is used as fuel, passes through a checkerwork of red-hot fire brick on its way to the furnace. The air, before it enters the furnace, is heated in the same way. Thus, a higher temperature is obtained in the furnace than could be produced by the use of cold gas and cold air.

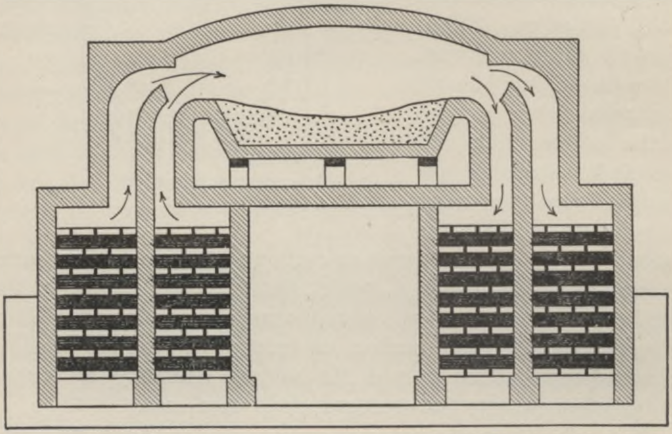


Fig. 57.—Regenerative furnace for the open-hearth process.

On their way out of the furnace, the products of combustion pass through two exactly similar checkerworks, which in about half an hour, are heated to a bright red heat. Then the direction of the gas and air is reversed. The cold gas and air on their way to the furnace pass through the heated checkerworks, the gas through one and the air through the other, while the other two systems are now heated by the hot gases from the furnace.

An open hearth furnace may hold fifty tons or more of melted metal. In order to utilize it, scrap steel is often added with the iron. The advantage of open hearth over Bessemer steel is that the process is under better control. The metal can be kept liquid on the hearth for hours; samples can be withdrawn and tested and additions of more pig iron or spiegel made if necessary. All this is impossible in the Bessemer converter, where the whole conversion is effected in twenty minutes and the metal freezes if there is any delay.

This means a large consumption of fuel and, accordingly, open hearth steel is a more expensive product than Bessemer steel, and is used for armor plate, heavy guns, machinery, boiler plates, railway bridges and so on. Many rails are now being made of open hearth steel and its use for this purpose is likely to become general. Increased speed and increased weight of both locomotive and cars have made it necessary to lay a tougher rail.

199. Water Gas.—Red-hot carbon acts upon *steam* as it does upon other oxides.

$$H_2O + C \longrightarrow CO + H_2 - 28{,}300 \text{ cal.}$$

In a steel cylinder lined with fire brick (Fig. 58) a fire of anthracite or coke is raised to a white heat by a blast of air introduced below the grate. This takes about ten minutes. Then the air is shut off and steam injected below the grate. The above equation shows that the resulting gas would contain, if pure, 50% by volume of carbon monoxide and 50% by volume of hydrogen. In practice, it also contains some carbon dioxide and nitrogen. The thermochemical symbols show that the reaction absorbs much heat. Hence the injection of the steam can only be continued five minutes, when the fuel-bed becomes cooled to such an extent that the interaction no longer occurs satisfactorily. Then the steam is stopped and the air blast restored.

The product is called *water gas.* It burns with a blue flame. In order to make the flame luminous, it is passed downward through a second cylinder called the "carburetter" (Fig. 58) in which it comes into contact with a spray of petroleum, and then upward though a third cylinder called the "superheater," which is packed with a checkerwork of red-hot fire brick. In the superheater the vapor of the petroleum is converted into gases which cause the water gas to burn with a luminous flame. The illuminating gas of the large cities of the United States is largely made in this way. However, at present the development of mantle-lighting has made the light-giving quality of the gas flame unimportant. It is the heat value of the gas which counts at present, for the gas which liberates the largest number of calories when it burns will heat the mantle to the highest temperature, and so produce the most light.

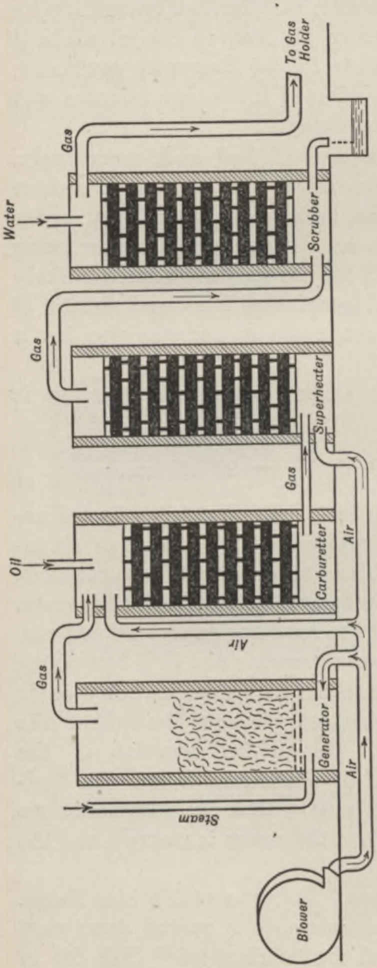


FIG. 58.—The manufacture of water gas.

200. Producer Gas.—Interrupting the production of gas every five minutes, in order to heat up the fuel bed, can be avoided by admitting *a certain amount of air with the steam.* The air burns some of the fuel to carbon monoxide:

$$C + O \longrightarrow CO + 29{,}300 \text{ cal.},$$

and the heat liberated compensates for the cooling effect of the reaction between the carbon and the steam.

This is the way in which the great quantities of *fuel* *gas* used about steel works and similar places are made. Such a gas will contain by volume, about

30% carbon monoxide
15% hydrogen
5% carbon dioxide
50% nitrogen

The jet of steam is made to suck in the required quantity of air, on the principle of the Bunsen burner. The gas is easily and cheaply made from coke, anthracite, or even bituminous coal, and has a high heat value.

BOOK III

THE ATOMIC THEORY.—IMPORTANT COMPOUNDS CONTAINING HYDROGEN

INTRODUCTION

We have seen that the kinetic theory, which explains the properties of gases by the assumption that they consist of molecules in rapid motion, has practically become a fact, owing to the irresistible evidence recently brought to its support. We must now enquire whether the molecule is a simple, indivisible mass, or whether it is a *structure*, composed of smaller particles. This question will be investigated in Chap. XII. Chap. XIII will be devoted to the compounds which hydrogen forms with sulphur and with nitrogen, and Chap. XIV to a few of the compounds of carbon and hydrogen, of which more than two hundred are known at present. In Chap. XV we shall study a class of compounds containing carbon, hydrogen and oxygen, which are abundant in nature and of great practical importance.

CHAPTER XII

THE ATOMIC THEORY

201. Atoms.—Carbon dioxide is composed of molecules, all of which are exactly alike. If, then, we could catch a single molecule, and analyze it, it would contain the same proportions of carbon and oxygen which are found in measurable quantities of the gas, that is, 12 parts of carbon and 32 parts of oxygen by weight. A molecule of carbon dioxide is not a simple particle, but a *group of smaller particles* which move about without parting company, and these smaller masses of which the molecule consists are of two kinds, particles of carbon and particles of oxygen.

The same statement is clearly true of all gases which are chemical compounds, like carbon monoxide, sulphur dioxide and steam. Their molecules must be composed of groups of particles of the elements of which they consist. But most solids and liquids can be converted into gases, by applying the proper temperature and pressure. Therefore, we can make a general statement that the molecules of all chemical compounds must consist of groups of smaller particles of the corresponding elements. To these smaller particles the name *atoms* is given. Atoms are the constituents of molecules. There are as many *kinds* of atoms as there are elements, that is, about eighty.

202. Value of the Atomic Theory.—The atomic theory gives a clear and simple account of the laws of chemical change, which we have hitherto regarded purely as facts.

The most fundamental fact in our science is, that *there are such things as atomic weights*, that is, that *there is, for each element, a number of parts by weight in which it is present in all of its compounds.* By means of these numbers, and small multiples of them, the composition of all chemical compounds can be expressed.

According to the atomic theory, these numbers are the relative weights of the atoms. Thus the atom of carbon weighs three-fourths as much as the oxygen atom. If, as the basis of our system, we take the arbitrary number 16 for the atomic weight of oxygen, the atomic weight of carbon becomes $16 \times \frac{3}{4}$ or 12. Carbon monoxide contains 12 parts of carbon to 16 of oxygen by weight. Its molecule, then, contains one atom of carbon (weighing 12) and one atom of oxygen (weighing 16). Since every atom of carbon weighs 12 and every atom of oxygen weighs 16 the proportions of carbon and oxygen in every molecule of carbon monoxide will be the same. Any measurable quantity of carbon monoxide is simply a very large number of such molecules and its composition will be the same as that of a single molecule. Hence the *law of definite proportions;* that the composition of a compound is constant. The same compound always contains the same number of the same kind of atoms in its molecule. Since each of these atoms has a constant weight, the composition of the molecule, and therefore of the compound, must be constant

203. Multiple Proportions.—Carbon *dioxide* contains 12 parts of carbon to 32 of oxygen and has the formula CO_2. It contains twice as much oxygen, for the same weight of carbon, as the monoxide. This is an instance of multiple proportions. When carbon monoxide burns, the carbon atom, which is already combined with one oxygen atom, takes on another. No less than a complete additional atom can be added, because the atoms are not divisible (from ἄτομος, indivisible)

204. Compounds of Sulphur and Oxygen.—Study of many sulphur compounds shows that the atomic weight of sulphur is twice as great as that of oxygen: hence if we assign the number 16 to the latter, sulphur assumes the value 32. The synthesis of *sulphur dioxide* (p. 94) shows that it contains equal weights of its two elements; hence the formula must be SO_2. A molecule must contain one atom of sulphur united with two of oxygen. *Sulphur trioxide,* which contains 48 parts of oxygen united with 32 of sulphur, receives the formula SO_3. Its molecule contains four atoms, one of sulphur and three of oxygen.

The symbols, which we have been using to denote the chemical unit quantities of the elements, can be read as meaning *atoms* of the elements. The symbol S may be used to mean 32 grams of sulphur, or as meaning an *atom* of sulphur which weighs 32, if the atom of oxygen weighs 16.

We have been using the *formulas* of compounds to denote weights of them which are produced by the union of the chemical unit weights of the elements. In the case of gases we have noted the surprising fact (p. 110) that the weights represented by the formulas of the different compounds fill the same volume under the same temperature and pressure (22.4 liters at S.T.P.).

The formula can just as well be used to indicate a *molecule* of the compound. Thus SO_2 may be used to mean (a) 32 grams of sulphur united with 32 grams of oxygen to form 64 grams of sulphur dioxide, which fill a volume of 22.4 liters at S.T.P.; or, it may mean (b) a group of three atoms, one of sulphur and two of oxygen, combined to form a molecule of sulphur dioxide. These two meanings are not so different as might at first sight be supposed. The numbers (atomic weights) remain the same and so, therefore, do the relative quantities in which the elements are present. Since actual chemical work is always done with weighable quantities, (a) is usually the more important meaning to bear in mind. The student will now perceive the reason for the use of the terms *atomic and molecular weight.* The abbreviation *mole* is employed for the molecular weight in grams. Thus:

64 grams is a mole of sulphur dioxide, SO_2.
44 grams is a mole of carbon dioxide, CO_2.
18 grams is a mole of water, H_2O.
88 grams is a mole of iron sulphide, FeS.
216 grams is a mole of mercuric oxide, HgO.

We have seen (p. 110) that the volume of the mole is the same for all gaseous compounds, 22.4 liters at S.T.P. In fact, if we were investigating a new gas, whose chemical composition was entirely unknown, we could nevertheless determine its molecular weight by getting the weight of 22.4 liters at S.T.P.

With liquids and solids, the volume of the mole is different for each substance.

205. The Relation between the Mole and the Molecule.— It happens that the mole of *pyrite* ($FeS_2 = 120$ grams) is just twice the mole of *quartz* ($SiO_2 = 60$ grams). The weights of the molecules, if the oxygen atom equals 16, are represented by the same numbers (120 and 60), so that the weight of each molecule of the pyrite is twice as great as that of each molecule of the quartz. Then the mole of pyrite must contain the same number of molecules as the mole of quartz. We take twice as much of the pyrite to make a mole, but each molecule is twice as heavy, so the number of molecules in the mole is the same.

It also happens that the mole of mercuric oxide ($HgO =$ 216 grams) is 12 times that of water ($H_2O = 18$ grams). Again the moles of the two substances must contain the same number of molecules. For we take twelve times as much of the mercuric oxide, but each molecule of it weighs twelve times as much as each water molecule.

From these examples it is easy to see that *the moles of all substances contain the same number of molecules.*

Calculations made by very different methods agree that the number of molecules in a mole cannot be far from 6×10^{23} (i. e. 6 followed by 23 ciphers). In order to get a rough idea of the vastness of this number, let us imagine that a mole (216 grams or about half a pound) of mercuric oxide is heated in such a way that a million molecules are decomposed into mercury and oxygen every second. It would be *twenty thousand million years* before the change was complete. This is about four million times the total period that has elapsed from the dawn of history to the present time.

The same calculations make the probable diameter of simple molecules, like those of hydrogen and oxygen, about one ten-millionth of a millimeter. This is about $\frac{1}{2000}$ the wave-length of violet light. The circles in Fig. 59 represent the diameters of the molecules of some familiar substances, magnified ten million times. The circles do not represent the shape in any way. Magnified on the same scale, a human red blood-corpuscle would be a disc 70 meters in diameter.

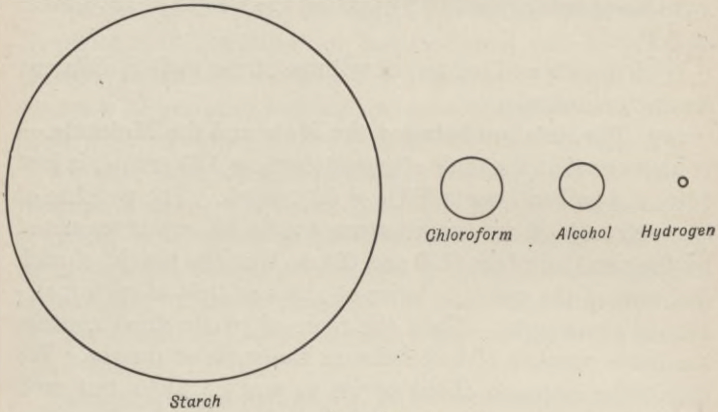


FIG. 59.

206. Moles of the Elements.—The weight of a liter of oxygen at S.T.P. is 1.429 grams. Then the weight of a mole of oxygen, 22.4 liters, must be

$$1.429 \times 22.4 = 32 \text{ grams.}$$

Accordingly, the mole of oxygen contains two chemical unit weights of 16 grams and the *formula* (not the symbol) of oxygen is O_2. Since we can read the mole formula directly as a molecule formula, this means that the molecule of oxygen gas is a group of two oxgyen atoms.

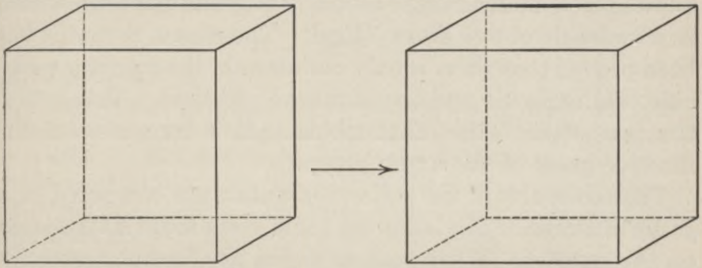
The weight of a liter of hydrogen at S.T.P. is .09 gram. The weight of the mole is

$$.09 \times 22.4 = 2.016 \text{ grams.}$$

Since the chemical unit of hydrogen (atomic weight) is

1.008, the formula is H_2. The hydrogen molecule is a group of two atoms.

This is always a difficult point. In order to attain perfect clearness upon it, think of a mole of carbon dioxide, 44 grams, occupying, at S.T.P., 22.4 liters. Now imagine the 12 grams of carbon removed. A mole of oxygen, 32 grams, would remain and the volume would be unchanged. Since equal volumes of gases contain equal numbers of molecules, this shows that the number of molecules has remained the same —each molecule of carbon dioxide has yielded a molecule of oxygen. Since each molecule of carbon dioxide contains two atoms of oxygen, each molecule of oxygen must contain two oxygen atoms. Representing the volumes by cubes $\frac{1}{10}$ the side and $\frac{1}{1000}$ the capacity of those which would be required to contain the gases, we have:—



A mole of carbon dioxide. A mole of oxygen.

As a matter of fact, we have seen that carbon dioxide does contain its own volume of oxygen (p. 99). Exactly the same argument can be used with sulphur dioxide.

Now think of a mole (28 grams) of carbon monoxide, CO, occupying 22.4 liters at S.T.P. Remove the 12 grams of carbon. 16 grams, or one-half a mole, of oxygen remain, which will fill 11.2 liters. From Avogadro's hypothesis it follows that the number of molecules of oxygen is half as great as that of the carbon monoxide molecules. The atoms of oxygen, as they were set free from the carbon monoxide, have united in pairs and again we find that *an oxygen molecule contains two atoms.*

207. Molecular Equations.—Substances are found to enter into chemical changes in the quantities represented by the chemical formulas, that is, in moles. Or, in the language of the atomic theory, chemical changes take place between molecules.

It follows from this that chemical equations ought, in strictness, to be written so that all the substances are present as molecules. A single atom has no right to appear unless the molecule of that substance really contains only one atom. Some of the equations we have been using do not satisfy this requirement. We can now revise them.

Inexact Form	*Revised Form*
$CO + O \longrightarrow CO_2$	$2CO + O_2 \longrightarrow 2CO_2$
$SO_2 + O \longrightarrow SO_3$	$2SO_2 + O_2 \longrightarrow 2SO_3$
$H_2 + O \longrightarrow H_2O$	$2H_2 + O_2 \longrightarrow 2H_2O$
$HgO \longrightarrow Hg + O$	$2HgO \longrightarrow 2Hg + O_2$

It will be noted that, in the last equation, the mercury is allowed to remain as single atoms (2 Hg) and not represented as a molecule of two atoms (Hg_2). The reason is that it has been proved that there is only one atom in the mercury molecule: the molecule and the atom are identical. This is also the case with all the other metals. It is true, also, of the inactive gases of the argon group.

The molecules of the *active non-metals* are composed of a *group* of atoms. The following table gives some information on this subject. When read as moles, the formulas give the number of grams which are (or would be) contained in 22.4 liters at S.T.P. In terms of the theory, they express the number of atoms in the molecule of the various substances:

Name	*Symbol*	*Atomic Weight*	*Formula*
1 **Oxygen**	O	16	O_2
2 **Nitrogen**	N	14	N_2
3 **Hydrogen**	H	1.008	H_2
4 **Chlorine** .	Cl	35.5	Cl_2
5 **Phosphorus**	P	31	P_4
6 **Sulphur**	S	32	At low temperatures S_8 At a red heat S_2
7 **Mercury**	Hg	200	Hg
8 **Carbon**	C	12	Unknown

208. Discussion of the Table.—In the study of chemistry, we should never be satisfied with a mere knowledge of the facts. The essential thing is to get a firm grasp of the *process* by which the facts are obtained —the *evidence* on which they are based. Let us discuss the table briefly from this point of view.

The student will be ready to accept the formulas of the first four elements without comment. They are gases, and he knows that, to find the molecular weight, we have only to weigh a liter at S.T.P. and multiply by 22.4. Thus, the weight of a liter of chlorine gas (Chap. XVI) at S.T.P. is 3.17 grams. Then the weight of the mole (molecular weight) is,

$$3.17 \times 22.4 = 71.$$

The atomic weight of chlorine is 35.5 (see table on inside of back cover). Hence the number of atoms in the molecule is

$$71 \div 35.5 = 2,$$

and the formula is Cl_2.

Sulphur cannot be obtained in the state of gas or vapor at S.T.P. It can, however, be obtained as vapor at a higher temperature, and the weight of a liter determined. From this weight by methods which are discussed in Chap. XXX, the weight of 22.4 liters of sulphur vapor at S.T.P. can be calculated. The same method can be employed with phosphorus and with mercury, but not with carbon.

209. Molecular Weights of Dissolved Substances.—Until the close of the 19th century the only way to determine the molecular weight was to weigh the gas or vapor of the substance. A great step in advance was taken by *Raoult* when he made it possible to determine the molecular weight of *dissolved* substances (Chap. XX). Thus *sulphur* dissolves in carbon disulphide and, from the behavior of the solution, the molecular weight of the dissolved sulphur can be ascertained. It is found, like sulphur vapor, to have the formula S_8. These methods are valuable in dealing with substances which cannot be converted into vapor. Sugar, for instance, yields no sugar gas when heated, but chars and passes into new substances. But by dissolving it in a suitable liquid, its molecular weight can easily be obtained.

When a solid substance can neither be vaporized nor dissolved without chemical change, its molecular weight remains unknown. The substances to which we have given the formula ZnS, FeS, Fe_3O_4 and Fe_2O_3 are of this kind. There is no way, at present, of determining the weight of the molecules of these compounds. We therefore use the simplest formula which will express the chemical composition. Fortunately, this is sufficient for all practical purposes.

210. Practical Advantages of Molecular Equations.—We have seen that chemical equations give a complete account of the proportions by weight according to which chemical changes occur. Plainly this knowledge is essential to the proper carrying out of any chemical process. Let us now see what additional information is contained in *molecular* equations, that is, in those which we have revised so that free atoms do not appear in them. For the combination of hydrogen and oxygen, we have:

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

Equal volumes of gases contain equal numbers of molecules. Hence the equation means that:

$$\begin{matrix}\text{2 volumes}\\ \text{of hydrogen}\end{matrix} + \begin{matrix}\text{1 volume}\\ \text{of oxygen}\end{matrix} \longrightarrow \begin{matrix}\text{2 volumes of steam}\\ \text{(above } 100^\circ\text{).}\end{matrix}$$

Since two molecules of hydrogen and one molecule of oxygen yield two of steam, the volume of the steam (above 100°) is equal to that of the hydrogen at the same temperature and pressure. The *total* volume is reduced by the combination in the ratio of 3 : 2.

Below 100° (p. 117), the steam condenses and the liquid water occupies a volume which is very small compared with that of the gases which produced it. This volume is easily calculated. Reading the equation in moles we have:

$$\begin{matrix}\text{4 grams hydrogen}\\ \text{44.8 liters}\end{matrix} + \begin{matrix}\text{32 grams oxygen}\\ \text{22.4 liters}\end{matrix} \longrightarrow \text{36 grams water.}$$

Since the specific gravity of water is unity, the volume of the 36 grams of liquid would be 36 c.c. This is only $\frac{1}{1800}$ of the volume of the gases (67,200 c.c.) which combined to form it. The eudiometer (p. 117) for lecture-experiments on this subject is usually graduated to $\frac{1}{5}$ c.c. Assuming that we exploded 30 c.c. of the mixed gases, the volume of the liquid water would be:

$$30 \times \frac{1}{1800} = \frac{1}{60}\text{c.c.},$$

which could not be measured. This explains why it is disregarded in actual work.

From Avogadro's hypothesis it is plain that in any equation dealing with *gases,* the coefficients giving the numbers of molecules can be directly read as though they represented *volumes.* The equation:

$$2CO + O_2 \longrightarrow 2CO_2$$

indicates, among many other things, that

$$\begin{array}{c}\text{2 volumes}\\ \text{carbon monoxide}\end{array} + \begin{array}{c}\text{1 volume}\\ \text{oxygen}\end{array} \longrightarrow \begin{array}{c}\text{2 volumes}\\ \text{carbon dioxide.}\end{array}$$

Suppose that an open hearth furnace (p. 148) is heated with producer gas containing 25% of carbon monoxide. What volumes of gas and air should be admitted to it to give complete combustion? For every cubic meter of oxygen we need 2 cu. m. of carbon monoxide. Since each cubic meter of air contains 0.2 cu. m. ($\frac{1}{5}$ of its volume) of oxygen, to get one cubic meter of the latter we need $\frac{1}{0.2}$, or 5 cu. m. of air. To get the 2 cu. m. of carbon monoxide, we must take $\frac{2}{0.25}$ = 8 cu. m. of producer gas. So that the equation indicates that the gas and air should be used in the ratio 8 : 5 by volume. Since an excess of oxygen is necessary, more air than the theoretical proportion would be admitted in practice.

Questions about the volumes of gases liberated during chemical changes can be quickly answered from the molecular equation, e. g.: What volume of oxygen, measured at S.T.P., will be produced when 9 grams of mercuric oxide are heated?

$$\begin{array}{ccccc}2HgO & \longrightarrow & 2Hg & + & O_2\\ \text{432 grams} & & & & \text{22.4 liters}\end{array}$$

Evidently the answer is:

$$\frac{22.4}{432} \times 9 = 0.467 \text{ liter or } 467 \text{ c.c.}$$

How much mercuric oxide must be heated to make a liter of oxygen at S.T.P.? The solution is:

$$\frac{432}{22.4} = 19.3 \text{ grams.}$$

On account of their greater simplicity, we shall continue, in some cases, to use equations in which free atoms appear.

Related Topics

211. Review.—We have seen (pp. 154–6) that the atomic theory gives a simple explanation of the four great laws of chemical combination by weight. Let us state these laws again, in the language of the theory.

1. *The law of definite proportions.* The molecules of the same compound are all alike. They contain the same number of atoms of the same kind. The weights of these atoms are constant.

2. *The law of multiple proportions.* Suppose that, into the molecule of a compound AB we introduce more of one element B, while the quantity of the other element A remains the same. Since the atoms are not divided we must introduce at least an additional atom of B, and the new compound will be AB_2.

3. *The law of the indestructibility of matter.* It is an experimental fact that the weight of a sealed vessel is not altered by any process (chemical or otherwise) which takes place in it. Theoretical statement: Atoms cannot be created nor destroyed. Chemical changes merely alter the way in which they are grouped to form molecules. However, recent advances in our knowledge of radium, and other radio-active substances, have decidedly changed our views with respect to the complete permanence of the atom (Chap. XXVII).

4. *The atomic weights.* The experimental fact: there is a natural chemical unit for each element; a number of parts by weight in which it enters into combination. By means of these numbers, and small whole multiples of them, the composition of all compounds can be expressed.

A moment's thought will show that this statement really includes the three laws just stated. For:

(a) If iron and sulphur unite always according to fixed numbers (56 : 32), the composition of iron sulphide must always be the same.

(b) Since sulphur always enters into compounds as a quantity of 32 parts, if we introduce more sulphur into iron sulphide we must introduce 32 additional parts. Hence pyrite (FeS_2) must contain twice as much sulphur, for the same weight of iron, as iron monosulphide (FeS).

(c) 56 parts of iron unite with 32 parts of sulphur to form a molecular weight ($56 + 32 = 88$ parts) of iron sulphide. Plainly, nothing is gained or lost in the combination. So that, in this case, the law of the indestructibility of matter is simply the fact that the molecular weight of a compound is the sum of the atomic weights of its elements.

Theoretical statement: The atomic weight numbers are simply the relative weights of the atoms. The number 16 is *assigned* to the oxygen atom, and the other numbers are calculated upon that basis.

212. The Law of Combining Gas Volumes.—Chemical interactions take place between molecules, and the number of interacting molecules is always small. Since equal volumes of gases contain equal numbers of molecules, if

1 molecule of a gas A interacts with 1 molecule of a gas B,
1 volume of A will interact with 1 volume of B.

If 2 molecules of A interact with 1 molecule of B
2 volumes of A will interact with 1 volume of B,

and so on. According to Avogadro's hypothesis, there must always be a simple relation between the volumes of the two gases. This is the theoretical statement of the law of combining gas volumes.

213. Historical.—*Democritus* (5th century B.C.) declared that matter was composed of particles which he called atoms, and that between them was empty space. Twenty-three centuries elapsed before *John Dalton*, of Manchester, in 1803, conceived that these atoms must have definite relative weights, which could be determined by the analysis of compounds. Recent investigations so strongly confirm the statement that matter has a granular structure, that it must be regarded at present as an established fact. We have just seen that the theory explains perfectly the laws of chemical combination. One thing, however, it leaves unexplained; the sudden change in all the properties of substances, which, as we have often pointed out, is the most striking feature of chemical changes. Why should the chemical union of mercury and oxygen yield a *red* powder? of copper and sulphur a *black* solid? of carbon and sulphur, both of which are odorless solids, a *strongly smelling liquid?* Countless questions of this sort might be asked. Every chemical process suggests one or more.

Definitions

Atoms. The smaller particles of which molecules consist.

Mole. The gram-molecular weight; the molecular weight, taken in grams.

CHAPTER XIII

COMPOUNDS OF HYDROGEN WITH SULPHUR AND NITROGEN.—LIQUEFACTION OF GASES.—REFRIGERATION

214. Interaction of Sulphur and Hydrogen.—When a glass tube containing 0.1 gram of sulphur and 100 c.c. of hydrogen is sealed and gently heated (300°) for a week, the sulphur disappears. When the tube is opened, a gas escapes which is clearly not hydrogen, for it has a powerful, unpleasant odor and it immediately blackens a clean piece of copper. Hydrogen is odorless and has no effect upon copper.

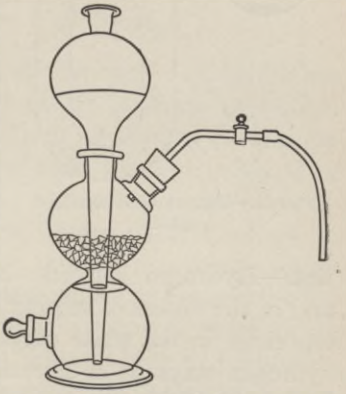


FIG. 60.—The Kipp apparatus.

This gas must be a compound of hydrogen and sulphur. It is therefore called *hydrogen sulphide.* Larger quantities of it can be obtained by the method described in the laboratory studies (interaction of iron sulphide and dilute hydrochloric acid). The Kipp apparatus (Fig. 60) is convenient. The interaction takes place according to the equation

$$\underset{\text{Iron Sulphide}}{FeS} + 2HCl \longrightarrow \underset{\text{Iron Chloride}}{FeCl_2} + \underset{\text{Hydrogen Sulphide}}{H_2S}.$$

215. Formula of Hydrogen Sulphide.—Hydrogen sulphide contains *its own volume* of hydrogen. This can be proved by the apparatus of Fig. 61. The flask is filled with hydrogen sulphide. There is a little tin in the bottom. The U-tube contains mercury covered with a layer of oil in the limb next the flask.

By the cautious application of a flame to the bottom of the flask, the tin is gently warmed. It combines with the sulphur, liberating the hydrogen, which is found, after cooling, to occupy the same volume as the hydrogen sulphide. This means that a mole of hydrogen sulphide contains a mole (2.016 grams or two chemical unit weights) of hydrogen. In other words, the molecule of hydrogen sulphide contains two atoms of hydrogen. For each molecule has yielded a molecule of hydrogen, and we have seen that the latter contains two atoms.

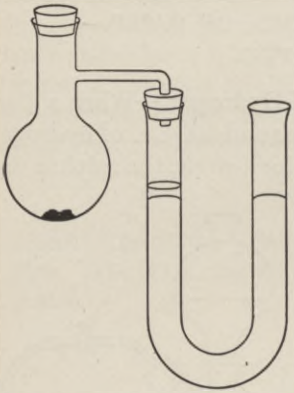


FIG. 61.—Heating tin in hydrogen sulphide.

A liter of hydrogen sulphide weighs, at S.T.P., 1.522 grams. Hence the weight of the mole is 1.522 × 22.4 = 34.08 grams. Subtracting the 2.016 grams of hydrogen we have left 32.06 grams of sulphur in the mole. Since this is one atomic weight of sulphur, *the formula of hydrogen sulphide is* H_2S.

216. Occurrence and Properties.—Hydrogen sulphide is contained in volcanic gases and in the waters of sulphur springs. Eggs contain sulphur, especially in the white portion, and, when they decompose, hydrogen sulphide is liberated. This is the cause of the odor of rotten eggs. A trace of hydrogen sulphide escapes when a boiled egg is opened, even though the egg is perfectly fresh.

Hydrogen sulphide is a colorless gas which, by cold and pressure, has been converted into a colorless liquid and into an ice-like solid. A liter of water at room temperature dissolves about 3 liters of it, alcohol twice as much.

Hydrogen sulphide burns with a blue flame, the hydrogen to water, the sulphur to sulphur dioxide. The latter is easily recognized by its odor; the water by the dew which deposits when the flame is allowed to burn in a cold bottle. When the flame is cooled by placing a porcelain dish or a glass plate in it, sulphur deposits upon the cold body.

At a red heat, hydrogen sulphide is decomposed. When it is led through a heated glass tube, sulphur deposits, while hydrogen passes on. It follows that, when hydrogen sulphide is burned, it must separate into its elements before union with oxygen occurs. This explains the deposit of sulphur when a cold object is introduced into the flame.

217. Use of Hydrogen Sulphide.—When exposed to hydrogen sulphide, a piece of copper or silver at once becomes covered with a black film of sulphide:

$$Cu + H_2S \longrightarrow CuS + H_2.$$

Many other metals behave in a similar way. Sulphides are formed also, when hydrogen sulphide is made to bubble through water in which compounds of certain metals are dissolved. Thus, distilled water, when allowed to stand in contact with lead, acts chemically upon the metal and dissolves traces of lead compounds. Some natural waters do the same. On account of the intense poisonous action of lead, it is often important to ascertain whether a water has dissolved any lead compounds from the lead pipes which are frequently used in plumbing. This can be done by passing hydrogen sulphide through the water by means of a glass tube. If the water contains even as little as a milligram of lead per liter—one part in a million parts of water—its presence is revealed by a dark-brown precipitate of lead sulphide. In water containing a dissolved *cadmium* compound, hydrogen sulphide produces a bright yellow precipitate of *cadmium sulphide*, CdS. Many of the other metal sulphides are insoluble in water and are formed in a similar way. For this reason hydrogen sulphide is constantly used in the laboratory in the detection of the metals and their separation from each other.

218. Action upon the Body.—Hydrogen sulphide is *poisonous*. In working with it, care should be taken to inhale as little as possible. The coloring matter of the red corpuscles is an iron compound called *hæmoglobin.* Hydrogen sulphide removes the oxygen from the corpuscle:

$$H_2S + O \longrightarrow H_2O + S$$

and, at the same time, converts the iron into iron sulphide. The blood, therefore, becomes incapable of supplying the body with oxygen.

219. Hydrogen Disulphide.—Hydrogen disulphide, H_2S_2 is a yellow oil, which separates into hydrogen sulphide and sulphur when preserved. It is of no special significance, but the corresponding oxygen compound, *hydrogen peroxide,* H_2O_2, has important applications (Chap. XXIV).

220. Ammonia: Preparation.—The familiar *ammonia-water,* so much used in the household, is a solution of ammonia gas in water. The gradual escape of the gas is the cause of the sharp odor of the liquid. Like most other dissolved gases, it escapes almost completely when the solution is heated and one method of preparing ammonia-gas is based upon this fact. Some steam is mixed with the gas prepared in this way, but this can be removed by passing it through a tube filled with small lumps of lime. This absorbs the water, forming *slaked lime,* while the dried ammonia gas passes on.

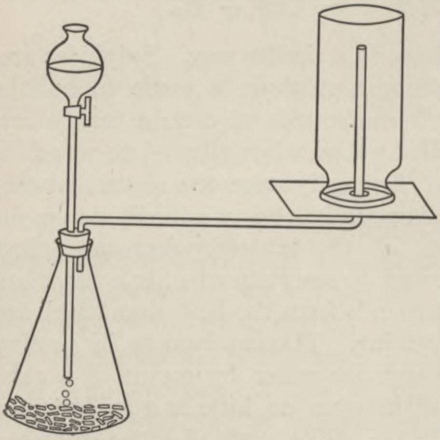


FIG. 62.—Preparation of ammonia gas from ammonia water.

A better method is to allow ammonia-water to fall from a dropping funnel upon caustic potash (Chap. XX). Being very soluble in water, the caustic potash absorbs the water, and the ammonia gas is set free in dry condition (Fig. 62). On account of the solubility of the gas in water, water cannot be used for collecting it.

Down to 1770, water was the only liquid employed for collecting gases, and those which were freely soluble in it were absorbed and escaped detection. About that time it occurred to Priestley to try mercury and he at once discovered a number of gases, among which were ammonia and sulphur dioxide. Hydrogen sulphide had been discovered by Scheele a few years before.

221. Physical Properties.—At room temperature, a pressure of about seven atmospheres converts ammonia into a colorless liquid. The same result is obtained, under ordinary pressure, by cooling to –34°. This liquid is largely used in ice-machines. Ammonia is one of the very soluble gases. Water dissolves at 0° more than 1000 times its volume, and at ordinary temperatures, about 700. The strongest ammonia-water of commerce has a specific gravity of about 0.9 and contains about 35% of ammonia by weight.

222. Composition.—When a mixture of nitrogen and hydrogen is treated with electric sparks the odor of ammonia appears. On the other hand, when ammonia itself is "sparked," its volume is doubled and the gas is found to consist of nitrogen and hydrogen.

Two conclusions follow:

1. Ammonia is a compound of nitrogen and hydrogen.
2. The reaction,

$$\text{nitrogen} + \text{hydrogen} \rightleftarrows \text{ammonia}$$

under the influence of electric sparks, proceeds forward or backward according to the concentration. So long as the percentage of ammonia in the gas is *less than three*, nitrogen and hydrogen unite; but in pure ammonia or in any gas containing more than three per cent of it, ammonia is decomposed into nitrogen and hydrogen.

In order, then, to make nitrogen and hydrogen unite completely, we must "spark" the mixture in such a way that the ammonia is removed as fast as it is formed. This is easily done by confining the gases in a eudiometer over dilute sulphuric acid, which at once absorbs the ammonia, forming with it a compound we shall study later (Chap. XXII). When a mixture of one volume of nitrogen with three volumes of hydrogen is treated in this way, all gas disappears and the liquid slowly rises to the top of the tube. Remembering that the nitrogen molecule is N_2 and that of hydrogen H_2, it follows that the molecule of ammonia contains three atoms of hydrogen for one of nitrogen—the *simplest* formula is NH_3.

That this is the *correct* formula is shown by the determination of the weight of 1 liter of ammonia at S.T.P., which is 0.76 gram. The molecular weight must be:

$$0.76 \times 22.4 = 17$$

and this corresponds to the formula NH_3.

223. Chemical Properties.—When a tube, from which ammonia is escaping, is held near the Bunsen flame, the ammonia burns in the Bunsen flame, with a yellowish color, but does not continue to burn when the flame is withdrawn. The explanation is that, like other hydrogen compounds, the ammonia must be decomposed by heat before the hydrogen can burn:

$$2\ NH_3 \longrightarrow N_2 + 3H_2.$$

The hydrogen then burns to water, while the nitrogen is liberated. In oxygen, ammonia burns with a continuous flame, which has a high enough temperature to separate the gas into nitrogen and hydrogen, and thus to provide the fuel necessary to its own existence.

Ammonia is decomposed by a red heat, according to the equation just given. When it is led through a hot glass tube, the mixture of nitrogen and hydrogen which collects is combustible and occupies twice the volume of the ammonia.

224. Occurrence.—The atmosphere contains traces of ammonia. Natural waters sometimes contain it. There is never enough to be harmful—less than one part per million by weight—but its presence is often an indication that the water has been recently contaminated by sewage, and may contain the typhoid germ.

Ammonia is produced during the decay of animal and plant matter. For this reason its odor is usually noticeable around stables, cesspools and manure-piles. The same fact explains the occurrence of ammonia in the soil, which always contains it. It is an important plant-food, but it cannot be absorbed by the roots until after it has been oxidized to *nitric acid* (Chap. XXIII).

225. Source and Uses.—*Bituminous coal* contains about 2% of nitrogen with much larger quantities of hydrogen. It is not surprising, therefore, that, when coal is distilled for the manufacture of illuminating gas or of coke, ammonia is always produced. This is the source of all of the ammonia of commerce.

The use of liquid ammonia for refrigeration has been mentioned. Ammonia water is widely used for scouring and cleansing. The use of ammonia gas in the manufacture of washing soda is important (Chap. XXIV). Great quantities of compounds containing ammonia (Chap. XXII) are used as fertilizers.

226. Other Compounds of Nitrogen and Hydrogen.—*Hydrazine*, N_2H_4, is a colorless liquid, which smells like ammonia, which it strongly resembles in properties.

Hydrazoic acid, N_3H, is a colorless liquid with an intolerable smell. It is highly explosive. It differs widely from ammonia in properties, being more like hydrochloric acid than ammonia in chemical behavior.

Related Topics

227. The Liquefaction of Gases, the Nature of Liquefaction.—The chief distinction between liquids and gases is that the molecules, at ordinary pressures, are more crowded in the former. While 3×10^{22} molecules fill a liter in the state of gas, the same number of molecules in the liquids is crowded into a volume which, on the average, would hardly be greater than a cubic centimeter. According to the kinetic theory, it is the rapid straight-line motion of the gas molecules which keeps them distributed evenly and prevents them from settling to form a layer of liquid on the bottom of the vessel. This motion is *heat*.

This suggests three methods of liquefying gases:

(a) To rob the molecules of their heat motion by **cooling.**

(b) To crowd the molecules closer by **pressure.**

(c) To combine (a) and (b), applying **pressure and cold together.**

When these conclusions are tested by experiment, it is found that:

(a) All gases could indeed be liquefied by cooling, were it not that the temperature required is often so low that it is difficult or impossible to reach it. Thus, sulphur dioxide, under one atmosphere pressure, liquefies at –8°, which can easily be obtained by merely mixing ice and salt. But hydrogen, under air-pressure, requires a temperature of –253°, while helium only assumes the liquid state at –268°.5, which is within 4°.5 of the absolute zero of Physics.

Fig. 63.—A Faraday tube.

(b) The effect of pressure alone upon gases has been discussed. § 90 should be re-read.

(c) The only possible conclusion is that, in most cases, it is necessary to apply pressure and cold simultaneously. This method, after much brilliant work, has led to the liquefaction of all gases. Helium was the last to yield.

228. The Faraday Tube.—*Michael Faraday*, in 1823, was the first to attack the problem in a systematic way. He employed a bent sealed tube of thick glass, called, after him, the "Faraday tube" (Fig. 63). In one limb was placed the mixture generating the gas which he desired to liquefy. The other limb was placed in a freezing mixture. The pressure was furnished by the continued production of the gas in a closed space. Faraday had no difficulty in liquefying sulphur dioxide, ammonia, carbon dioxide, hydrogen sulphide and many other gases by this simple method. Others, like hydrogen, nitrogen, and oxygen, showed no evidence of liquefaction.

229. Liquefaction of Oxygen.—The method used by *Pictet* (Dec. 22, 1877) in liquefying oxygen was the same in principle as that of Faraday. The gas was generated in a strong wrought iron retort and forced, under its own pressure, into a metal tube closed by a stopcock. By means of solid carbon dioxide (the evaporation of which was made more rapid by an air-pump) this tube was cooled to –140°. Liquid oxygen escaped when the stopcock was opened.

Recent experimenters have largely worked along the same line as Pictet, but they have used powerful pumps to compress the gases and have employed more efficient methods of cooling.

230. Self-intensive Cooling.—When a compressed gas is allowed to expand freely, it becomes a little cooler. There is a slight attraction between the molecules of gases, and energy is used up in separating them. The effect is slight—less than 1° —yet by a simple device due to *Linde*, the cooling can be *accumulated* until the gas becomes a liquid. A diagram of Linde's apparatus is shown in Fig. 64. Air is compressed to 200 atmospheres and the heat produced is removed in a water-jacketed cooler. It then passes through P_2 into the liquefying apparatus which consists simply of a double copper tube. The compressed air passes down through the inner tube into the

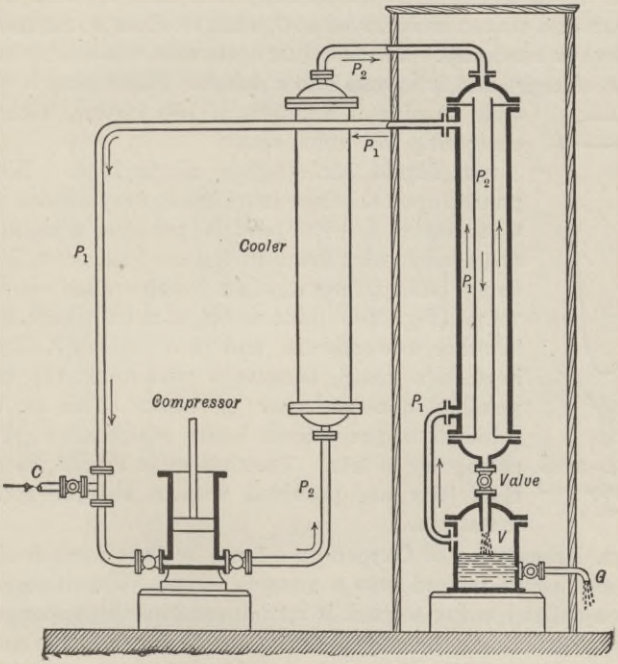


Fig. 64.—Preparation of liquid air.

vessel V, where it expands and is slightly cooled (say 1°). Taking the temperature of the room as 20°, that of the expanded gas is 19°. From V, it follows the upward arrows through P_1 to the space between the outer and inner tubes. Thus the freshly compressed air in P_2 on its way to V is cooled by the colder expanded air. This second quantity of gas will have a temperature of 19° *before* it expands and will drop to 18° afterward. Thus the temperature in the liquefier falls until, after an hour or so, liquid air can be removed at G, while fresh air is introduced at C when necessary. In the actual apparatus, the double tube is not straight, but is wound into a spiral. This makes it possible to give it a length of 100 meters, without occupying too much space.

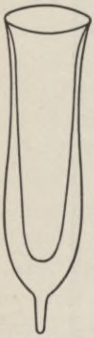


FIG. 65.—A vacuum-jacketed vessel.

231. Liquid Air.—*Liquid air* is blue. When poured upon the floor it instantly evaporates. Its temperature is –192° and it produces a cloud of condensed water drops in the air, just as ice does. It can be kept for hours in a double-walled vacuum vessel (Fig. 65). Like water, it must absorb heat in order to evaporate, and heat reaches it slowly in such a vessel, because a vacuum is the best possible non-conductor of heat. This is the principle of the *vacuum bottles*, which have grown so popular of late. They resemble Fig. 65, except that they are provided with a stopper and a metal case.

232. Preparation of Oxygen on a large Scale.—Some freshly liquefied air is poured into a vacuum vessel. From time to time a splint bearing a spark is introduced into the upper part of the vessel above the surface of the liquid. At first the spark is extinguished. The nitrogen is escaping. After the vessel has stood for a time, the spark when introduced is relighted, showing that the gas now escaping contains much more oxygen than ordinary air. The explanation is that the boiling-point of nitrogen (–194°) is lower than that of oxygen (–182°). Hence the nitrogen, being the more volatile liquid, evaporates most rapidly. This is additional evidence that *air is a mixture.*

From the boiling-point of the two gases, it will be seen that if Linde's apparatus (Fig. 64) is run in such a way that only a fraction of the air is permanently condensed, that fraction will be chiefly oxygen. Oxygen is now made commercially chiefly by this method, which is cheap because, with the exception of the coal needed to run the engine for the pumps, the atmosphere is the only raw material required. Liquid air, made by Linde's method, is allowed to trickle over glass balls packed in a tall column. The nitrogen evaporates and passes off through a tube at the top, while liquid oxygen collects at the bottom.

There is a large field for oxygen in illumination and in metallurgy, but the high price of the gas has hampered its applications. It is likely that the Linde method will reduce the price to a point at which it will become possible to employ oxygen for many practical purposes. The product contains some nitrogen (about 5 %), but that does not interfere seriously with its use.

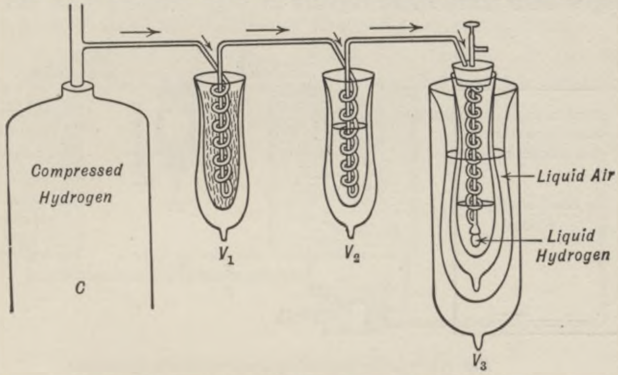


FIG. 66.—The liquefaction of hydrogen

233. Liquefaction of Hydrogen: Some Results.—Since Linde's invention, self-intensive cooling and external cooling have often been combined in low-temperature work. The apparatus used by Dewar in the liquefaction of *hydrogen* (1898) is an illustration (Fig. 66). C is a cylinder containing pure hydrogen under a pressure of 200 atmospheres. V_1 V_2 and V_3 are vacuum-jacketed vessels (Fig. 65). V_1 contained solid carbon dioxide, V_2 liquid air boiling rapidly in a partial vacuum. Thus, before self-intensive cooling was begun, the hydrogen was cooled to

–205°. V_3 was empty. It was sunk in a larger vacuum vessel containing liquid air. The principle is the same as that of Fig. 64. Liquid hydrogen collected in V_3. Its properties have been discussed (p. 116).

The lowest temperature thus far reached is –271°.5. This is within 1°.5 of the total absence of heat. *Onnes* obtained this temperature by boiling liquid helium in a partial vacuum.

Most bacteria are rapidly killed by temperatures in the neighborhood of 100°, but they are very resistant to cold. Long exposure to the temperature of liquid air has no destructive action upon them.

We have noticed the very important fact that all chemical changes take place more rapidly at high temperatures than at low. *At temperatures in the neighborhood of –200° the speed of almost all chemical processes becomes so small that they may be considered as not occurring at all.* Substances which interact violently at room temperature remain in contact without any apparent change.

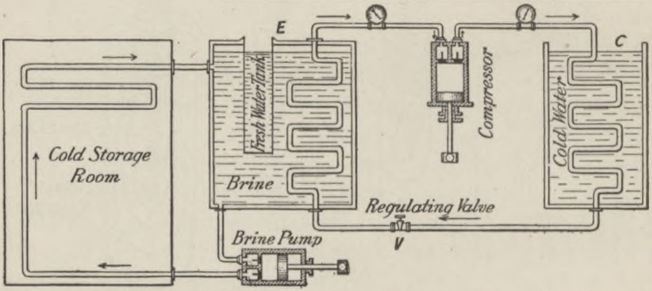


Fig. 67.—Artificial cooling and ice-making apparatus.

234. The Ammonia Ice Machine.—All liquids absorb much heat when they evaporate. *Refrigeration by machines* is based upon this fact. Liquid ammonia has largely displaced other liquids because it is cheap and because, when it becomes ammonia gas, it absorbs large quantities of heat, 300 calories for every gram which evaporates.

The diagram (Fig. 67) will make clear the principle of the ice machine. The ammonia gas is forced, by a pump operated by a steam engine, into a coil of iron pipe, *C*, where it condenses, liberating 300 cal. of heat for every gram of liquid formed. This heat is removed by water circulating outside the coil. The liquid ammonia passes through a regulating valve into a second coil, *E*, which is immersed in a tank of brine. Here, aided by the suction of the same pump, it evaporates, absorbing 300 calories of heat per gram. Hence the brine becomes cold. If tin cans containing water are hung in it, the water will be frozen. In cold-storage warehouses, the chilled brine is circulated in iron pipes through the rooms to be cooled. Dwellings might be supplied with chilled brine from a central station, where the ice-machine for the entire neighborhood was placed. This brine, passing through a coil in the box where foods were kept, would make a clean and efficient substitute for the ordinary refrigerator. The entire house could be cooled, during hot weather, in the same way, but the expense has thus far prevented the application of the method.

CHAPTER XIV

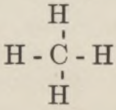
COMPOUNDS OF CARBON AND HYDROGEN

235. Marsh-Gas.—When the rotting vegetable matter on the bottom of a marshy pool is stirred, bubbles of *marsh-gas* escape. Fig. 68 shows an easy method of collecting the gas. It is colorless and combustible, burning, when a lighted match is applied to it, with a pale blue flame, not unlike that of hydrogen. However, if we burn a test-tube of the gas and then at once shake up some lime-water in the tube, the liquid becomes milky. *Carbon dioxide* has been produced by the combustion. This proves that marsh-gas is a *carbon compound.*

FIG. 68.—Collection of marsh-gas.

A current of marsh-gas which has been carefully dried is passed through a glass tube and lighted at the orifice. When a dry cold bottle is held over the flame, a dew composed of fine drops of water deposits. Marsh-gas, then, is a compound of carbon and *hydrogen.* Careful investigation shows that when pure it contains only these two elements.

Quantitative work shows that marsh-gas contains 12 parts of carbon combined with 4.032 parts of hydrogen by weight. This points to the formula CH_4. The weight of a liter of pure marsh-gas is 0.716 gram. Multiplying this by 22.4 we get 16.03 as the molecular weight. This leaves no doubt that CH_4 is the correct formula. It is often written more fully thus:



$$\begin{array}{c} H \\ | \\ H - C - H \\ | \\ H \end{array}$$

This does not indicate the *shape* of the molecule of marsh-gas. It means simply that the carbon atom is in the center and that around it are grouped four hydrogen atoms, each of which is united to the central carbon atom in the same way.

236. **Methane.**—The chemical name of marsh-gas is *methane.* It has been converted into a colorless liquid which has a specific gravity of only 0.41. Liquid hydrogen (spec. grav. 0.07) is the lightest of liquids and liquid helium (spec. grav. 0.15) is next. Liquid methane comes third. **Natural gas,** by which whole cities in Pennsylvania, Ohio and West Virginia are heated, is chiefly methane (90%).

Like all combustible gases, methane forms an explosive mixture with air. This mixture is the *fire damp* (from the German word *Dampf,* vapor) of the coal mines. Accidents caused by fire damp are especially frequent in mines where bituminous coal is obtained.

237. **Coal Gas.**—Methane makes up about one-third by volume of *coal gas* which is much used for lighting in Europe and in smaller American cities. Coal gas is made by distilling soft coal in cylindrical fireclay retorts (Fig. 69). Since the coal does not distill as *coal,* but is destroyed or broken up, by the white heat applied, into simpler substances, the process is called *destructive* distillation. The residue left in the retorts is **coke**.

The result is a complex mixture. Recalling that soft coal contains much carbon and hydrogen, along with oxygen, sulphur and nitrogen, we might expect, among the substances we have studied, the following to be formed:

Hydrogen
Methane
Carbon monoxide
Carbon dioxide
Carbon disulphide
Hydrogen sulphide
Ammonia

All of these substances and many others are, in fact, produced. The last three in the list above must be carefully removed from the gas before use, for they would cause it to produce an unpleasant odor when burned. Many liquid and solid compounds of carbon and hydrogen are formed, and these must be removed, since they would clog up the pipes. The purified gas varies in composition, according to the coal and the temperature. An average is the following:

1. Hydrogen 45% by volume
2. Methane 33% by volume
3. Other compounds of carbon and hydrogen 5% by volume
4. Carbon monoxide 14% by volume
5. Nitrogen 3% by volume

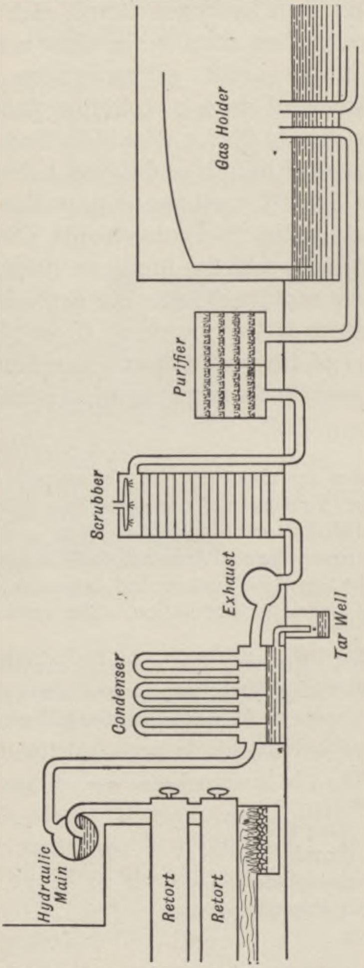


FIG. 69.—Manufacture of coal gas.

We shall examine into the nature of the compounds in (3) shortly. One metric ton of good coal yields about 300 cu. m. of gas (1 cu. m. = 35.3 cu. ft.).

238. Manufacture of Coal Gas.—The process of the manufacture of coal gas is best understood from the diagram (Fig. 69). From the *retort* a tube takes the gases up to the *hydraulic main*. This is a horizontal pipe running at right-angles to the retorts. Here much liquid and solid matter collects. The rest is removed by the *condenser*, a long series of iron pipes with a box at the bottom for the collection of oily and tarry products. These, with the material from the hydraulic main, flow into the *tar well* and make up the mixture called *coal tar*. An exhaust now transfers the gas to the *scrubber*, a tall iron tower in which water trickles down over coke or wooden slats to remove the ammonia and hydrogen sulphide. Then follows the *purifier*, an iron box with perforated shelves, filled with ferric oxide. The gas then goes through a meter into the holder, from which it is distributed to the consumers.

239. Hydrocarbons of Coal Gas.—A compound of carbon and hydrogen is called a *hydrocarbon*. Since hydrogen, carbon monoxide and methane all burn with a pale blue flame, the light-giving quality of coal gas must be due to the five per cent. of hydrocarbons mentioned in (3) §237. This five per cent. is made up roughly as follows:

Acetylene,	C_2H_2	1.5%	by volume
Ethylene,	C_2H_4	2.5%	by volume
Benzene,	C_6H_6	1 %	by volume

Methane, CH_4, contains 75% by weight of carbon: these three hydrocarbons contain more, as the formulas show. Ethylene contains 86% and acetylene and benzene (which clearly have the same percentage composition) contain over 92% of carbon by weight. All three are decomposed by the heat of the flame, before they combine with oxygen, and the fine particles of solid carbon which separate glow brightly; hence the light.

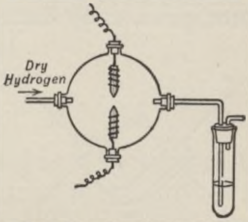


Fig. 70.—Synthesis of acetylene.

240. Acetylene.—When hydrogen is slowly passed through a globe in which the electric arc is burning between carbon poles, *acetylene* is formed (Fig. 70). The reaction is strongly endothermic:

$$2\,C + H_2 \longrightarrow C_2H_2 - 58{,}000 \text{ cal.}$$

Acetylene can be easily made by the interaction of water and *calcium carbide*. This is a hard iron-black solid which may be familiar to the student from its use in automobile and bicycle-lamps. It is a chemical compound of carbon with a metal, *calcium*, which we shall study later. One kilogram of the commercial carbide, brought into contact with water, yields about 300 liters of acetylene. Automatic apparatus is constructed by which the carbide is gradually fed into a large volume of water. The gas is purified and stored in small gas holders.

241. **Properties.**—Acetylene is a colorless gas with an unpleasant smell. When mixed with air it explodes violently on contact with flame. It is readily liquefied by pressure alone, but the liquid is a dangerous explosive. Endothermic compounds, which, like acetylene, are formed from their elements with *absorption* of energy, are, in most cases, explosive. The explosion of liquid acetylene (in absence of air) is simply sudden separation into hydrogen and carbon. The energy which was absorbed in the combination is violently liberated.

242. **Use.**—On account of its richness in carbon, acetylene produces a sooty flame when an ordinary burner is used with it. A good burner for it is shown in Fig. 71. Air is drawn in through the side-holes on the Bunsen principle. The two flames strike each other and broaden out into a single flame at right-angles to the plane of the burner. This flame is intensely bright and its light resembles sunlight closely: hence the acetylene light is excellent for judging colors. A liter of acetylene gives about as much light as twenty liters of coal gas. It is much used for illumination in the country, in localities remote from a gas-works. Copper gas-holders or pipes must not be used in handling acetylene, for it forms a highly explosive compound in contact with this metal.

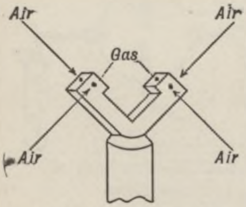


FIG. 71.—A burner for acetylene.

243. **The Acetylene Blowpipe.**—The combustion of any hydrocarbon results in the production of carbon dioxide and water. Acetylene, burning in oxygen, produces the hottest flame known. Its temperature is close to that of the electric

arc (nearly 4000°). The reason becomes clear when we consider that the gas is an endothermic compound. The 58,000 calories, which are absorbed when acetylene is formed from its elements, are again liberated when it is decomposed in the flame. When acetylene burns, we obtain 100,000 cal. for each of the two atomic weights of carbon, 70,000 cal. for the two atomic weights of hydrogen, and, in addition, the 58,000 cal. from the decomposition of the gas before it burns. So the thermochemical equation is:

$$C_2H_2 + 5\ O \longrightarrow 2CO_2 + H_2O + 328{,}000\ \text{cal.}$$

The burner employed is shown in Fig. 72. It is often called the *oxy-hydrogen blowpipe*, because it was first used with hydrogen and oxygen. It consists of an inner tube, conveying the oxygen, surrounded by a larger one which carries the acetylene. The burner does not melt because the base of the flame is comparatively cool. The oxy-acetylene flame is much used in working metals. A six-inch shaft of solid steel has been cut in two with it in less than forty seconds, while, in another test, a circle twenty inches in diameter was cut out of one-inch steel plate in forty-five seconds.

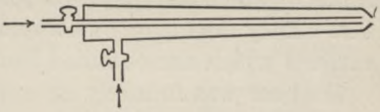


FIG. 72.—The oxy-hydrogen blowpipe.

244. Benzene.—When acetylene is passed through a hot tube some of it is converted into *benzene*.

$$3\ C_2H_2 \longrightarrow C_6H_6\ .$$

Benzene (which must not be confused with the benz*i*ne from petroleum) is a colorless liquid which takes fire readily, burning with a smoky flame. It is formed by the distillation of soft coal, and some of it passes as vapor into the coal gas, but most of it collects, as a liquid, in the hydraulic main and the condenser, and is found in the coal tar.

245. Naphthalene, Anthracene.—Two other hydrocarbons of coal tar must be mentioned on account of their commercial importance.

Naphthalene, $C_{10}H_8$, is known commercially as "moth balls," "tar balls" and "tar camphor." Coal tar contains nearly ten per cent. of it. It is contained in coal gas and sometimes causes trouble in winter by condensing in the pipes and clogging them. It crystallizes in white shining plates which have a tarry smell.

Anthracene, $C_{14}H_{10}$, forms colorless glistening leaflets. It is important because it is used for the manufacture of the important dye-stuffs which were formerly obtained from the *madder* plant. Large quantities of benzene and naphthalene are used for the manufacture of drugs, perfumes, photographic developers and dye-stuffs. These substances, thousands of which have been prepared, are not *contained* in coal tar. They are made, by complex processes, from the hydrocarbons which are obtained from the tar by distillation.

Coal tar was formerly an annoying waste-product of the gas-works. At present they are unable to supply enough to meet the increasing demands of chemical industry. Fortunately, the rational manufacture of coke (p. 43) is a great and growing source of coal tar.

246. Petroleum.—Petroleum is an oily liquid found in the rocks in certain localities, especially in Pennsylvania, Ohio, Texas and California. It also occurs in Russia near Baku on the shore of the Caspian Sea, where vast quantities have been obtained from an area of only six square kilometers.

When a well is first drilled, thousands of barrels of petroleum often spout from it per day. Later the pressure subsides and the petroleum is pumped to the surface. It is distributed to the refineries by iron pipe-lines, which, in the United States, have a total length of many thousand miles. The world's production of petroleum is about 35 million tons each year, of which the United States furnishes two-thirds.

247. Formation and Nature of Petroleum.—Petroleum was probably formed from great accumulations of animal and vegetable remains by a slow change in which a moderately high temperature and great pressure played an important part. All petroleums are mixtures of hydrocarbons. Pennsylvania petroleum is composed of hydrocarbons which resemble methane closely in chemical properties, and are therefore said to belong to the same *series*. The following table gives a partial list of these hydrocarbons, with their boiling-points and an indication of their uses:

Name	*Formula*	*Boiling-point*	*Commercial Name*	*Use*
Methane	CH_4	—160°	Natural gas	Fuel
Ethane	C_2H_6	— 93°		
Profane	C_3H_8	— 45°		
Butane	C_4H_{10}	1°		
Pentane	C_5H_{12}	36°	Mixture of the two is called *petroleum ether*	Scouring and cleansing agent for cloth, etc., enriching water gas
Hexane	C_6H_{14}	69°		
Heptane	C_7H_{16}	98°	Mixture of hexane and heptane is called *naphtha* or *gasoline*	Scouring and as fuel
Octane	C_8H_{18}	126°	Mixture of octane and nonane is called *benzine*	Like gasoline, fuel for automobiles, motor boats, etc.
Nonane	C_9H_{20}	150°		
Decane	$C_{10}H_{22}$	173°	Mixture of these seven hydrocarbons in varying proportions is *kerosene*	Illuminating oil
to				
Hexadecane	$C_{16}H_{34}$	287°		
Eicosane	$C_{20}H_{42}$	Solid (melts at 37°)	Mixed with higher members is called *paraffine*	Candles, sizing, etc.
Hexacontane	$C_{60}H_{122}$	Solid (melts at 100°)		

An inspection of this table reveals three important facts:

1. The number of hydrogen atoms in any member can be obtained by multiplying the number of carbon atoms by two and adding two to the product. Hence the formulas need not be memorized.

2. The formula of any hydrocarbon can be obtained by adding one carbon atom and two hydrogen atoms (CH_2) to that of the hydrocarbon next below it in the series.

3. The melting- and boiling-points gradually rise as we ascend in the series, so that the first members are gases, the middle members liquids, and the higher members solids. From pentane on the names are formed by adding *ane* to one or two syllables of the Greek numerals.

248. **Refining.**—Some petroleums, especially those from Ohio, Texas and California, contain, with the hydrocarbons, compounds of sulphur and of nitrogen which make the refining difficult. Much oil of this sort is burned in the crude state, as fuel for steamships and locomotives. However, most petroleum is refined for use.

Refining is essentially a process of *distillation* in which the crude oil is separated into a number of fractions which differ from each other in boiling point and composition. No attempt is made to separate the hydrocarbons themselves in pure condition. This can be done, but it is too tedious and expensive for practical purposes. The fractions into which the crude oil is separated are still mixtures, but of a few hydrocarbons only.

The petroleum is distilled from a horizontal iron cylinder into a coil of pipe cooled by water. A thermometer, immersed in the vapor, controls the process. The chief fractions, with the temperatures between which they are collected, are indicated in the following table.

When the temperature rises to 300° the oil still remaining in the cylinder is distilled by the use of a higher temperature and is placed in a vessel where it is chilled by pipes containing brine from an ice-machine.

Commercial Name	*Composition*	*Temperatures*
Petroleum ether	$C_5H_{12} + C_6H_{14}$	40° to 70°
Gasoline	$C_6H_{14} + C_7H_{16}$	70° to 90°
Naphtha	$C_7H_{16} + C_8H_{18}$	90° to 120°
Benzine	$C_8H_{18} + C_9H_{20}$	120° to 150°
Kerosene	$C_{10}H_{22}$ to $C_{16}H_{34}$	150° to 300°

Paraffine separates in crystalline plates. The portion which remains liquid, in spite of the chilling, is used as *lubricating oil*, for which purpose it has largely displaced oils of animal and vegetable origin. Or, if instead of distilling and freezing out the paraffine, the liquid remaining in the cylinder is simply robbed of its dark color by filtering it hot through bone-charcoal, it forms a pasty mass which is used as a lubricant and ointment under the names *vaseline*, *cosmoline* or *petroleum jelly*.

The kerosene is further purified by shaking it with sulphuric acid and then with caustic soda solution (lye). It is from this fraction that the necessity of the refining can be most easily understood. If crude petroleum was put directly into a lamp, the lower hydrocarbons would mix with the air above the oil and cause constant danger of explosion, while the highest ones would clog the wick and give a smoky flame.

Gasoline, naphtha and benzine were formerly products for which it was difficult to find a ready sale. At present the automobile and the motor-boat have caused such a demand for them that they bring a higher price than the kerosene. *Since these three substances are often used for cleansing in the household, it should be noted that the greatest care must be taken to make sure that no flame or fire is in the house when such work is done. Shocking accidents often occur from slight carelessness in this respect.*

249. Ethylene Series.—*Ethylene*, C_2H_4, is a colorless gas which burns with a bright flame. It is the first member of a series of hydrocarbons:

Ethylene	C_2H_4
Propylene,	C_3H_6
Butylene,	C_4H_8, etc.

In this series, the number of hydrogen atoms is obtained by multiplying the number of carbon atoms by two. The three just named are gases, the middle members liquids, and the higher members solids like paraffine. They can readily be prepared from the corresponding members of the methane series.

250. Acetylene Series.—*Acetylene*, C_2H_2, heads a third series in which the number of hydrogen atoms is obtained by multiplying the number of carbon atoms by two and subtracting two:

Acetylene,	C_2H_2
Allylene,	C_3H_4
Crotonylene	C_4H_6

There are also many hydrocarbons related to benzene, C_6H_6. The total number of hydrocarbons known is upwards of two hundred, of which some are found in nature (methane series) but many are purely laboratory products. The number which *could* be prepared is almost unlimited.

251. Asphalt.—*Asphalt,* or "mineral pitch," is a hard, black, combustible solid with an odor recalling that of kerosene. On the island of Trinidad there is a lake of it 1½ miles in diameter, warm and soft in the center, but hard and cold near the edge. Asphalt is chiefly a mixture of hydrocarbons, but it also contains oxygen and sulphur. It is used in paving.

Definitions

Hydrocarbon. A compound of carbon and hydrogen.

Series. A group of related compounds, similar in composition and properties. The molecular weights gradually increase from one compound to the next.

CHAPTER XV

SOME COMPOUNDS CONTAINING CARBON, HYDROGEN AND OXYGEN

252. Starch Formation.—We have seen (p. 103) that, under the influence of light, the leaves of plants decompose the carbon dioxide of the air and give off oxygen. Unlike the oxygen, the carbon does not separate in the free state. It combines with water, which is abundant in plants, and forms *starch*, $C_6H_{10}O_5$, which may be regarded as resulting from the combination of six atoms of carbon with *five molecules of water*.

The solution of *iodine* which is used for the external treatment of sprains and other injuries affords a delicate test for starch. The result of bringing the two together is an intense blue color. By the aid of this test, the fact that starch is produced in the green portions of plants, when acted upon by light, can be shown. A nasturtium plant, for instance, is kept in the dark for a time, and a portion of a leaf is protected by fastening tin foil on both sides of it. The plant is then exposed to light for some hours. The leaf is picked and soaked, after removing the tin foil, in alcohol, which dissolves the green coloring matter, turning the leaf white. It is then transferred to a dilute solution of iodine, where in a short time it turns bright blue wherever the light had access. The portion which was protected by the tin foil remains white, showing that no starch was formed there.

253. Properties.—*Starch* is a white powder, composed of little grains called "starch granules," the size and shape of which differ in different plants. It is possible, therefore, to determine with the microscope the plant from which a given sample of starch has been derived. It is an important element in food, being largely contained in grains like rice, oats, rye and wheat. Ordinary flour is about three-fourths starch.

Potatoes, peas, beans and many other vegetable products contain large quantities of it. Starch does not dissolve in cold water; with hot water, it forms a paste.

254. Oxidation of Starch.—Under proper conditions, starch can be oxidized to carbon dioxide and water. A glance at the formula shows that the molecule contains just enough oxygen to convert the hydrogen into water. We need, therefore, twelve atoms of oxygen for the six carbon atoms:

$$C_6H_{10}O_5 + 6O_2 \longrightarrow 6CO_2 + 5H_2O + 680{,}000 \text{ cal.}$$

The great production of heat should be noticed. It is largely by the oxidation of substances very similar to starch that the heat of the animal body is maintained.

255. Source of the Energy of Life.—Plainly the equation for the reduction of carbon dioxide to starch in the leaves of plants must be the reverse of the one just given, and 680,000 cal. must be *absorbed:*

$$6CO_2 + 5H_2O \longrightarrow C_6H_{10}O_5 + 6O_2 - 680{,}000 \text{ cal.}$$

This 680,000 calories furnishes the energy for all the life processes of animals and plants. Every process in the animal body occurs with a *loss* of energy, and this is true of plant processes also, with the single exception just noted. Just as the energy to run a clock is supplied only in the winding, so the energy which runs the life processes of organic nature is supplied solely by the reduction of carbon dioxide by plants. We may well call this the most important of all chemical processes.

Since the reduction does not take place in the dark, it is clear that the energy must be absorbed from *sunlight.* Experiments made by growing plants under variously colored transparent screens have shown that it is mainly the yellow rays in the neighborhood of the green that produce the effect. It is a curious fact that these same rays are also the most effective in acting upon the retina in the production of vision.

256. Extraction and Uses of Starch.—Starch is extracted chiefly from potatoes in Europe and from corn in the United States. The corn is softened by soaking it in water into which sulphur dioxide has been passed, and is then crushed. The pulp is placed upon a movable sieve of fine brass gauze and shaken under a spray of water. The starch granules pass through the sieve into a vat where the milky liquid is allowed to settle. A second filtration through fine silk gauze is necessary to remove plant fibres, which pass through the first sieve. Starch is used for laundry purposes, for making paste, for sizing, for the manufacture of glucose, etc.

257. Glucose.—When starch is boiled with very weak hydrochloric acid, it combines with a molecule of water and passes into *grape sugar* or *glucose*, $C_6H_{12}O_6$. The action of the hydrochloric acid is catalytic,

$$C_6H_{10}O_5 + H_2O \longrightarrow C_6H_{12}O_6$$

The hydrochloric acid—which would give the product a sour taste—is removed by adding the proper quantity of soda, which, as we shall see later, interacts with the hydrochloric acid, forming common salt, which, in small quantity, does not damage the product. The solution of glucose obtained in this way is a sweet, syrupy, yellowish liquid much used as a table-syrup, for the manufacture of candy, and as a substitute for malt in brewing.

Pure glucose is a white solid, very soluble in water. It belongs to a class of substances known as *sugars*, of which table sugar is the most familiar example. Glucose is sweet, but not as sweet as common sugar, and it does not crystallize as readily. Glucose is contained in the juices of most sweet fruits, for instance cherries and grapes. The sweet white incrustation, which often appears on raisins, is glucose.

258. Fruit Sugar or Fructose.—Grape sugar is usually accompanied in fruits by another sugar called *fruit sugar*, or *fructose*. The two sugars have exactly the same composition, $C_6H_{12}O_6$, but they differ in properties because the atoms are differently arranged. Fruit sugar is less soluble in water and much sweeter than grape sugar. Like the latter, it is white and crystalline.

259. Sucrose.—Common *sugar*, called cane sugar or *sucrose*, is one of the most important of all chemical products. Six million tons of it are obtained each year in Europe from the *sugar beet*, which is a variety of the common beet. Ordinary beets contain five per cent of sucrose, but in the sugar beet the quantity has been increased by cultivation to twenty per cent and has even reached twenty-seven per cent in certain specimens. It thrives in temperate regions with abundant sunlight. Germany, Austria, France and Russia are the chief producers of beet sugar, but the industry is growing in the United States.

The *sugar cane* is a species of grass which reaches a height of 2 to 6 meters and contains about twenty per cent of sucrose. It grows only in warm climates. Nearly nine million tons of sugar are obtained from it each year, chiefly in Louisiana, Texas, South America, Hawaii, and the East and West Indies, especially Cuba.

260. Extraction of Sugar.—In the extraction of sugar the cane is passed between heavy iron rolls which squeeze out the juice. This is boiled down in a closed vessel in the upper part of which a vacuum is maintained so that the boiling-point is only about 65°. The crystals which separate are dried in centrifugal machines. This brown impure "raw sugar" is shipped to the refinery, where it is dissolved and the syrup filtered through cloth bags to remove dust, plant fibre, etc., and then through layers of *bone black* to remove the coloring matter.

Bone black is charcoal made from bones. It contains only about ten per cent of carbon, the rest being the mineral matter of the bone, but it has a remarkable power of absorbing coloring matters from liquids.

When the syrup leaves the bone black filters, it is colorless. It is then boiled down in vacuum pans and dried in centrifugal machines. The drying of "granulated sugar" is completed in a steam-heated cylinder, kept in motion to prevent the crystals sticking together. A trace of ultramarine is added to the sugar to correct a yellow tint due to impurities.

The extraction of sugar from the beet is begun by cutting it into thin slices which are systematically treated with water to dissolve the sucrose. The purification of the beet-sugar is more complex than that of cane sugar, because the impurities occurring with it in the beet are more difficult to remove.

261. Properties of Sugar.—Sucrose crystallizes in colorless inclined prisms which are seen in almost pure condition in "rock candy." Sugar, salt and starch ("corn starch") are the only food products which are practically pure chemical compounds. Most foods are highly complex mixtures.

Sugar is very soluble in water, and, when the solution is boiled, the sucrose slowly takes up a molecule of water and passes into a mixture of equal parts of grape sugar and fruit sugar:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}.$$

This change becomes rapid in presence of traces of *hydrochloric acid* and other acids, which act catalytically. Syrup obtained in this way is used in candy making and for imitating honey. When it is mixed with 25% of real honey, it is difficult for the chemist to distinguish the mixture from the pure product of the bee-hive.

262. Carbohydrates.—Let us review the formulas of the compounds thus far studied in the present chapter:

Starch	$C_6H_{10}O_5$
Glucose	$C_6H_{12}O_6$
Fructose	$C_6H_{12}O_6$
Sucrose	$C_{12}H_{22}O_{11}$

It will be noted that these four substances all contain twice as many hydrogen atoms as they do oxygen atoms: that is, they contain hydrogen and oxygen in the proportions in which these two elements exist in water, H_2O. A compound containing hydrogen and oxygen in these proportions, united to carbon, is called a *carbohydrate*. Carbohydrates occur in animals, but they are especially characteristic of plants.

263. Cellulose.—The most abundant carbohydrate is *cellulose*, $C_6H_{10}O_5$. The formula is the same as that of starch, but it should be noted that in both substances the molecular weight is unknown; the formula is merely the simplest one which will express the composition.

Plant fiber and *wood fiber* are chiefly cellulose. *Linen, cotton, wood* and *paper* consist mainly of it. The best grades of filter paper are nearly pure cellulose. Pure cellulose is a soft white mass of fibers, insoluble in most liquids. Enormous quantities of cellulose are made from wood, for the manufacture of cheaper grades of paper. The wood, cut into small pieces, is heated in a closed vessel under pressure for several days with a liquid which dissolves the cement which holds the wood fibers together, but does not affect the cellulose. Paper containing much wood-fiber slowly turns brown, especially under the influence of light. The better papers are made of cotton or linen rags.

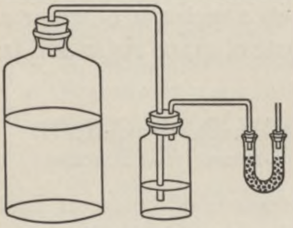


Fig. 73.—Fermentation.

264. Fermentation.—The fresh juice of grapes is sweet, on account of the presence of grape sugar. Heated and sealed up while hot, grape-juice remains sweet, but when kept without heating, it enters into *fermentation*. Countless gas bubbles escape and the sweet taste is replaced by the alcoholic flavor of wine. Examination of the liquid at this stage shows that it contains innumerable cells of a microscopic plant called *yeast*.

Further information can be gained by the apparatus of Fig. 73. The liquid contains about 100 grams of glucose, dissolved in a liter of water. A yeast cake, crushed in a little water, has been added. The small bottle contains limewater. The U-tube is filled with fragments of caustic soda to keep out the carbon dioxide of the air. The experiment proceeds most rapidly at about 30°.

The white solid which appears in the limewater proves that the gas, which escapes from the fermenting liquid, is *carbon dioxide.* The **alcohol** which remains in the large bottle can be separated by *fractional distillation.* Alcohol boils at a lower temperature (78°.5) than water. Therefore, when a mixture of alcohol and water is distilled, most of the alcohol is contained in the earlier portions which are collected.

Thus, if we distill 100 c.c. of the mixture, the *distillate* (as the liquid obtained by condensing the vapor is called) may contain enough alcohol to identify it by the taste and smell. Or, we can put the 100 c.c. into a small flask and distill 5 c.c. of it, and this second distillate will probably be rich enough in alcohol to burn.

The equation for the fermentation of glucose is:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Alcohol}}{2C_2H_6O} + 2CO_2.$$

Fructose ferments in exactly the same way, the equation being identical. Cane sugar does not ferment directly, but the yeast contains a substance called *invertase,* which acts just as hydrochloric acid does upon the sucrose (p. 195), converting it into glucose and fructose, which then ferment.

265. Alcohol.—*Alcohol,* C_2H_6O, is a colorless liquid with a pleasant odor and a. burning taste. Its specific gravity is 0.8. It freezes at –130° to a white mass. It mixes with water in all proportions, not forming two layers. Alcohol takes fire readily and burns with a blue flame. When it is burned in a cold dry bottle, water condenses in the walls and carbon dioxide can be recognized by the limewater test. Alcohol is used for making varnishes, lacquers, and important drugs, like chloroform, chloral and iodoform. Alcohol lamps with a mantle attached are employed in Europe for lighting. Pure alcohol is a violent poison. Dilute solutions (alcoholic beverages) are injurious but the effects are not so immediate.

266. Denatured Alcohol.—Although it costs only about thirty cents to make a gallon of alcohol, yet the price at which it sells is about ten times as much. The reason is that the government exacts a tax which amounts to about $2.07 per gallon. Alcohol intended, not for the production of beverages, but for the industries which require it, is *denatured*, that is, mixed with substances which give it a disgusting taste or render it more poisonous. Such alcohol is tax-free. The substances most frequently used to denature alcohol in the United States are 10% of wood alcohol and 0.5% of benzene. Since wood alcohol is excessively poisonous—being especially destructive in its action upon the eyes—denatured alcohol must not be employed in the preparation of anything which is to be taken internally, nor should it be used for bathing the body.

267. Diastase.—The starch which is stored up in seeds like wheat, rye and barley, acts as a supply of nourishment for the young plant until it is able to provide for itself. Now it is clear that the starch must be changed into something else before it can serve as plant food, for starch does not dissolve in watery liquids, like plant sap. It would remain inert in the roots, and could no more supply the stem and leaves of the young plant with carbon than could so much charcoal-powder. Nature solves this problem by the formation, during the sprouting of seeds, of a substance called *diastase,* which acts catalytically upon the starch and changes it to a sugar called *maltose,* which has the same composition as common sugar:

$$\underset{\text{Starch}}{2C_6H_{10}O_5} + H_2O \longrightarrow \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}.$$

268. Maltose.—*Maltose,* $C_{12}H_{22}O_{11}$, is not as sweet as sucrose. Like the latter, it dissolves freely in water and it can therefore be carried about in the plant juices and used where it is needed. Yeast transforms it to glucose and ferments the latter.

269. Malt Liquors, Beer, Ale and Stout.—*Malt* is made by moistening selected barley and allowing it to form a sprout nearly as long as the grain. The young plant is then killed by a gentle heat. When malt is crushed, and treated with warm water, the diastase rapidly changes the starch to maltose. The liquid is then boiled with hops to give flavor and keeping qualities.

After rapid cooling, the liquid is ready for fermentation. Pure yeast is added to it in vats of great capacity, made of oak. The yeast changes the maltose to glucose, which then ferments:

$$C_6H_{12}0_6 \longrightarrow 2C_2H_6O + 2CO_2 + 35{,}000 \text{ cal.}$$

The large evolution of heat makes it necessary to cool the vats, for in the fermenting of beer the temperature must not be allowed to rise above 5°. Brewing on a large scale only became possible with the invention of the ice-machine.

In the fermentation of *beer* the yeast grows at the bottom of the liquid and the finished product contains 3 to 5% of alcohol.[1]

In the manufacture of *stout* and *porter* a portion of the malt is heated hot enough to char it a little and produce brown coloring matters, which dissolve in the liquid.

Ale is fermented by a yeast which grows at the *top* of the liquid and requires a temperature near that of an ordinary room (15°–22°). Ale contains more alcohol than beer (up to 8%).[1]

270. Whiskey.—In the making of *whiskey*, rye or corn is crushed and heated gently with malt and water. The diastase converts the starch of both malt and rye into maltose which is then fermented by the addition of pure yeast. Fermentation stops before the liquid contains 17% of alcohol, for the yeast plant cannot work in strongly alcoholic liquids. The liquid is then subjected to fractional distillation, carried out in such a way that the distillate contains about 50% of alcohol by volume, the balance being chiefly water with small quantities of flavoring substances.

271. Production of Alcohol.—The production of *alcohol* is carried out in the same way, the chief differences being (1) that any cheap material rich in starch can be used (potatoes or corn), and (2) that distilling apparatus of such perfection is employed that it is possible to obtain 95%

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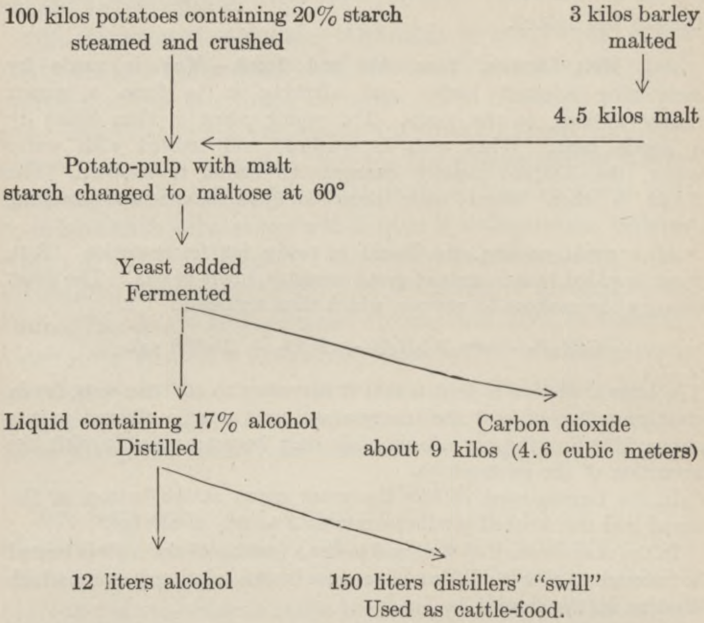
[1] Percentages of alcohol are stated by volume.

alcohol as a distillate. A diagram will make the matter clear and give an idea of the quantities employed.



272. Relation of Yeast to Fermentation.—When yeast cells are killed, their fermenting power is not destroyed. Thus, if yeast is dipped into a mixture of alcohol and ether, the cells are killed, for they will neither grow nor reproduce, but the dead yeast, when added to a glucose-solution, will cause rapid fermentation. When living yeast is ground with sharp sand, the cell walls are broken and the inside liquid escapes. By proper filtration, the liquid can be freed from yeast-cells. This sterilized liquid vigorously ferments glucose. These facts show that fermentation is not connected in any way with the *life* of the yeast plant. The part played by the cell is merely to produce and to store up a substance which acts catalytically upon the glucose, transforming it into alcohol and carbon dioxide. The name *zymase* has been given to this substance. It is white and soluble in water, but has not yet been obtained in pure condition.

273. Aldehyde.—Crude alcohol before it is purified by redistillation contains small quantities of *aldehyde*, C_2H_4O.

Pure aldehyde is a colorless liquid with a sharp odor, recalling that of apples. It can be made by cautiously heating alcohol with various mixtures which give off oxygen:

$$\underset{\text{Alcohol}}{C_2H_6O} + O \longrightarrow \underset{\text{Aldehyde}}{C_2H_4O} + H_2O.$$

274. **The Formation of Vinegar.**—When the bung is removed from a cask of wine, so that air has access, the liquid slowly turns to vinegar. Comparing the properties of wine with those of vinegar, we can reach the conclusion that the alcohol has been changed into an **acid** (we shall learn something about the properties of acids presently). In fact, vinegar does contain from 5 to 15% of *acetic acid.*

While the change of wine to vinegar is going on, the liquid contains great numbers of microscopic organisms called *acetic acid bacteria,* which change the alcohol to acetic acid, just as the yeast cells change glucose to alcohol.

Since the formation of vinegar requires the admission of air, we might conclude that the alcohol is *oxidized* to acetic acid. If so, the change ought to proceed rapidly when the air has freer access. This is the basis of the *quick vinegar process,* by means of which wine, or any other dilute alcohol, can be transformed into vinegar in a few hours.

A large cask, perforated with many holes to admit air, is packed with beechwood shavings, which are moistened with vinegar to infect them with the bacteria. Dilute alcohol, allowed to drip slowly through the shavings, is completely converted into vinegar in a very short time.

275. **Acetic Acid.**—*Acetic acid,* $C_2H_4O_2$, is a colorless liquid, which freezes, a little below room temperature, to an ice-like solid. It smells like vinegar and, when diluted with water, tastes like it. In contact with iron, zinc, magnesium and some other metals, it liberates *hydrogen.* It slowly converts dissolved cane sugar into glucose and fructose.

Litmus is a blue dye, obtained from a kind of moss. It dissolves in water and, when a drop of acetic acid is added to the blue liquid, the color at once changes to red.

276. Acids.—The statements just made are true not only of acetic acid but of other acids also. Thus we may define an acid as a substance having the following properties:

1. Its dilute water solution tastes *sour*.
2. It turns blue litmus solution red.
3. It converts cane sugar into glucose and fructose. *Active* acids, like hydrochloric acid, produce this change rapidly; *inactive* acids, like acetic acid, more slowly.
4. An acid is a *hydrogen* compound. Part or all of its hydrogen escapes when the water solution of the acid is treated with a metal like iron, zinc or magnesium. Other things being the same, *the more active the acid, the more rapidly the hydrogen is evolved.*

Acetic acid, in the dilute form of wine-vinegar, was the only acid known to the ancients. The so-called "mineral" acids, hydrochloric, sulphuric and nitric, were prepared by the alchemists during the middle ages.

277. Methyl Alcohol.—*Methyl alcohol,* CH_4O, is called *wood alcohol* because it is obtained by the distillation of wood (p. 41). It is purified by fractional distillation. It can be made from methane, but the method is not suitable for practical purposes. Pure methyl alcohol is a liquid resembling ordinary (ethyl) alcohol in appearance and odor. It boils at a lower temperature (66°). Its intense poisonous action has been referred to. When the quantity taken is too small to kill, it often produces total blindness.

Wood alcohol is used in making varnish, in the manufacture of dyes, in denaturing alcohol and in the manufacture of formaldehyde.

278. Formaldehyde.—*Formaldehyde,* CH_2O, is formed when a mixture of the vapor of methyl alcohol with air is passed over a hot spiral of copper wire:

$$CH_4O + O \longrightarrow CH_2O + H_2O.$$

It is a colorless gas with a penetrating, unpleasant odor. It is sold as a 40% solution in water under the name *formalin.* Formaldehyde is an excellent disinfectant, being rapidly fatal to all kinds of micro-organisms. It does not tarnish metal objects, nor bleach colored fabrics. It is almost the only disinfectant employed at present for fumigating rooms, clothing, furniture, etc. When added to milk, meat and other food products, formaldehyde prevents decay. Food preserved in this way is unwholesome and the use of formaldehyde, as a food preservative, is illegal.

279. Formic Acid.—*Formic acid,* CH_2O_2 is a colorless liquid with an irritating odor. It boils at 100°. It owes its name to its presence in ants (Latin, *formica*). It is also contained in the stinging hairs of the nettle.

When formic acid is allowed to drop into warm sulphuric acid, pure carbon monoxide escapes.

$$CH_2O_2 \longrightarrow H_2O + CO.$$

The sulphuric acid retains the water. This is the best laboratory method of making carbon monoxide.

Formic acid, owing to a new method of making it, has become cheap, and is being used instead of acetic acid in calico-printing and dyeing.

280. Series of Alcohols, Aldehydes and Acids.—Methyl alcohol is the first member of a *series* of alcohols. Ordinary (ethyl) alcohol is the second member. The general formula of the series is $C_nH_{2n+2}O$. Each member differs from the one below by the addition of one carbon and two hydrogen atoms (CH_2).

CH_4O methyl alcohol
C_2H_6O ethyl alcohol
C_3H_8O propyl alcohol, etc.

There is also a series of *aldehydes,* the general formula of which is $C_nH_{2n}O$

CH_2O formaldehyde
C_2H_4O ordinary aldehyde
C_3H_6O propyl aldehyde, etc.

Finally, there is a series of acids, the general formula of which is $C_nH_{2n}O_2$:

CH_2O_2 formic acid
$C_2H_4O_2$ acetic acid
$C_3H_6O_2$ propionic acid
$C_4H_8O_2$ butyric acid
. . . .
$C_{16}H_{32}O_2$ palmitic acid
$C_{18}H_{36}O_2$ stearic acid, etc.

Butyric acid gives the odor to rancid butter. *Palmitic* and *stearic* acids are important constituents of animal and vegetable fats and oils.

Definitions

Carbohydrate. A compound of carbon, hydrogen and oxygen, in which there are twice as many hydrogen atoms as oxygen atoms.

Fermentation. The change of a sugar to alcohol and carbon dioxide under the influence of yeast. In a general sense, the word applies to all chemical changes brought about by microörganisms.

Acid. A hydrogen compound which tastes sour, reddens blue litmus, converts cane sugar into glucose and fructose, and, when it interacts with metals like zinc or iron, liberates hydrogen.

BOOK IV

THE SODIUM GROUP OF ELEMENTS.—THE CHLORINE GROUP

INTRODUCTION

In Book IV we shall continue the plan we have followed thus far, of devoting our main attention to compounds containing only two elements. The starting-point of the work will be the *salt* of the household, which we shall prove, by laboratory and lecture-table experiments, to be a compound of a green suffocating gas called *chlorine* with a soft white metal *sodium.*

The natural continuation of our work with salt will be a study of the compounds of chlorine with the metals and nonmetals with which we are already familiar from the first three books. These compounds are known as *chlorides* and many of them are of decided scientific and commercial importance.

Turning to the chlorides of elements new to us, we shall take up a mineral called *sylvite* which is much like salt in taste and other properties. We shall not be surprised, therefore, to find that it is a compound of chlorine with a metal called *potassium* which is so similar to sodium that the compounds of the two can be profitably studied together.

The conclusion will be formed by the study of a group of elements which are remarkably similar to chlorine in chemical behavior.

CHAPTER XVI

TABLE-SALT: SODIUM AND CHLORINE

281. Rock Salt.—The *salt* of the household is a white powder, which consists of cubical crystals. Natural salt, called "rock salt" or *halite*, is an abundant mineral and is mined, especially in Germany and Austria. It occurs mixed with clay, gypsum and other substances, and must be purified for table use. Most of the impurities are insoluble in water. The rock salt is dissolved and the impurities allowed to settle. When the clear liquid is drawn off and evaporated in an iron vessel, a much purer grade of salt is obtained.

282. Salt Wells.—In our own country, extensive deposits of salt exist in New York, Ohio, Michigan, Kansas, Nevada and other states. The United States produces more salt than any other country, but very little of it is obtained by mining. It is chiefly made by boiling down the water of *salt springs*, which are abundant in the states just mentioned. When these natural brines do not flow from the earth, they are obtained by sinking wells and pumping. Often the brine is too poor in salt to be boiled down profitably. Then a hole is drilled into the salt-bearing rock, which always abounds in the locality, and the brine is run into it. When saturated with salt, it is pumped out and evaporated. At present, the evaporation is often done in large vacuum vessels, like those used in the sugar-refineries. The wet mass obtained by evaporation is fed in at the top of a large, inclined, revolving cylinder, heated by steam. A dry powder of salt runs out at the lower end.

283. Sea Salt.—In warm, dry regions, salt is obtained from *sea-water* by natural evaporation. At Giraud, near the mouth of the Rhone in southern France, large shallow basins are dug in the clayey soil of the strand of the Mediterranean. Sea-water is admitted in the Spring, and allowed to evaporate until saturated with salt. Meanwhile, clay and gypsum separate from it. The liquid is run into another basin, where the evaporation is continued until much of the salt has deposited. The crusts of salt are raked out and stood in heaps to drain. This salt averages about 95% in purity. When the deposited salt begins to be quite impure, the liquid is run into a third basin, in which a lower grade of salt is deposited.

The water of the open sea contains about 3.5% of solid matter of which about 2.5% is salt. The remainder consists of a great variety of substances. The water of some lakes is much richer in salt. The Great Salt Lake contains over 20% of salt. In such waters, aquatic life is impossible.

284. Salt Solution.—Salt *dissolves* in water. This means that, when thrown into water, it disappears, slowly if the liquid is left to itself, and rapidly if the vessel is shaken. A solid which behaves in this way is said to be **soluble** in water. The corresponding negative word is **insoluble.** The salt water obtained is called a **solution.** A solution may be colored but it is *clear*. An insoluble solid, like starch-powder or clay, can be dispersed through water by shaking, but the mixture will be *turbid*, like muddy water. A turbid mixture of a solid and a liquid is called a **suspension.** In time, the suspended matter will settle, leaving the liquid clear. Dissolved matter never settles.

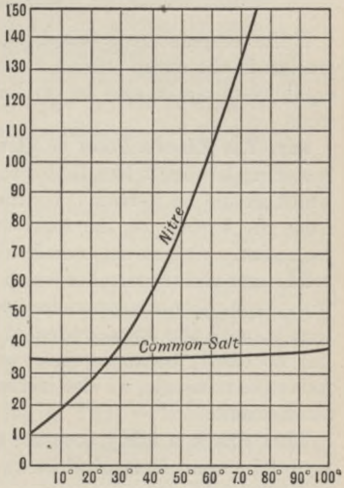


FIG. 74.—Solubility curves of salt and nitre.

By slowly adding salt to a measured volume of water it can be shown that there is a limit to the quantity which the water will dissolve. 100 grams of water at 0° will take up 35.7 grams of salt, and no more. The solution is then **saturated** and any more salt thrown into it will simply fall to the bottom and form a layer which, no matter how thick, does not increase the amount dissolved.

285. Effect of Heating on the Amount of Salt Dissolved.—By trying the same experiment at various temperatures it has been shown that the quantity of salt taken up by 100 grams of water increases slightly with rising temperature until, at 100°, nearly 40 grams of salt are dissolved. The results are most easily understood from a "**curve.**"

In Fig. 74 the distances measured from right to left indicate temperatures, while the distances upward represent grams of the solid dissolved by 100 grams of water. The curve for salt shows at once the slight but regular increase in solubility with rising temperature. The steep ascent of the curve for nitre (saltpeter) shows strikingly the much more rapid increase in the solubility of that substance.

Almost all solids are more soluble in hot water than in cold. There are a few exceptions to this statement. Slaked lime and a few other solids decrease in solubility when the temperature rises. This can be illustrated by boiling some limewater, which at once becomes turbid from the separation of some of the lime.

286. Application of the Idea of Concentration to Solutions.—It is plain that solution is merely another example of the controlling influence of *concentration* over chemical events. Pour water over sugar, and the sugar dissolves until its concentration in the solution attains a certain value. Then equilibrium results and no more sugar is taken up, even if the two substances are left in contact for years.

$$\text{Sugar (solid)} + \text{Water} \rightleftharpoons \text{Syrup (saturated)}.$$

If the temperature is raised, more sugar is taken up, until its concentration in the syrup attains a new value, higher than the old. Then equilibrium again sets in, so long as the temperature remains the same.

287. The Kinetic Point of View.—From the kinetic viewpoint, the reasoning is almost like that already given for gas solutions (p. 71), which should be re-read. We must think of sugar molecules escaping from the surface of the solid and moving about among the water molecules. At once sugar molecules begin to bombard the surface of the solid sugar and the number which returns to the solid state will increase with the number of sugar molecules in each cubic centimeter of the syrup, that is, with the *concentration* of the sugar. Throwing in more sugar has no effect, because, while we increase the opportunity of sugar molecules to escape, we also increase the chance to return to exactly the same extent.

That this is a fairly accurate picture of the real state of things is proved by many facts, of which two may be stated. From the formulas of sugar and water

$C_{12}H_{22}O_{11}$	molecular weight	342
H_2O	molecular weight	18

we see that there can be no reasonable doubt that the sugar molecules are larger and heavier than the water molecules. It follows that, *to a test of sufficient delicacy*, sugar-solution ought to behave like water with very fine solid particles suspended in it.

(1) When a beam of electric light is passed into pure water (free from dust) in a dark room, the path of the beam is invisible. But when pure sugar is dissolved in the pure water, the track of the beam of light becomes visible, just as it is in water containing very fine dust. This can only be due to the reflection of the light by the sugar molecules.

(2) Muddy water can be rapidly cleared by whirling it in a centrifugal machine. The particles of mud, being vastly heavier than the water molecules, go to the outside of the rotating vessel and collect there. Now solutions behave in exactly the same way. It is necessary to have a vessel divided into outer and inner compartments communicating by small apertures—otherwise the liquid will mix uniformly again as soon as the machine is stopped. When a solution is whirled rapidly in a vessel of this kind, the dissolved substance collects preferably in the *outer compartment,* and even separates in the solid state there, if the whirling is rapid enough.

288. Supersaturated Solutions.—100 c.c. of water at 100° dissolves nearly 500 grams of sugar but at 20° only 200 grams. When a solution of sugar which has been saturated at 100° is allowed to cool to 20°, about three-fifths of the sugar separates in crystals.

Let us take 100 c.c. of water and saturate it with sugar at 20°. It will take up 200 grams. We now heat the liquid to 100° and dissolve more sugar in it. It would take up 300 grams additional, but we add only a small fraction of this quantity, say 20 grams. The liquid is now cooled to 20° once more. Now if this liquid is kept quiet in a perfectly clean bottle, the separation of the extra 20 grams of sugar may not occur for a long time. Thus we have made a liquid which contains *more sugar than the saturated solution contains,* at the same temperature. Such a liquid is called a *super*-saturated solution. It can only exist so long as the solid which tends to separate is absent. When a crystal of sugar is let fall into our super-saturated solution, it at once drops the extra load of 20 grams in crystals, and the saturated solution is formed.

289. Composition of Salt: Flame Test.—When a bit of salt is held in the Bunsen flame by means of a clean iron wire or a pair of forceps, the salt does not burn, but it vaporizes and colors the flame intensely yellow. Many experiments have shown that this yellow color is due to the presence of a metal called *sodium.* Sodium itself and all its compounds produce the color. Among familiar sodium compounds which instantly color the flame bright yellow are soap, washing soda, baking soda, caustic soda and borax.

290. Sodium.—*Sodium,* then, is one of the elements of salt. It is a *light* metal, having about the same specific gravity as water, and is soft enough to be easily cut with a knife. The freshly cut surface has a bright, pinkish-white metallic luster which disappears at once, for sodium rusts in the air far more rapidly than the ordinary metals. It is a good conductor of the electric current and the high price of copper has led to the proposal to use sodium—enclosed in iron tubes—for the conduction of electric currents. As we shall see, the iron is necessary to protect the sodium from water and air. Sodium was first prepared by Sir Humphry Davy in 1807.

Heated in the absence of air, sodium melts, at a little below 100°, to a liquid which looks like mercury. It boils at a red heat, passing into a blue vapor, the specific gravity of which shows that the sodium molecule contains *but one atom.* This seems to be the case with the molecules of all the metals. The symbol of sodium is Na, from the German name *natrium.*

Heated in air, sodium takes fire easily and burns with a bright yellow flame to sodium oxide. In air which has been carefully dried, it ignites with great difficulty—another instance of the catalytic action of water vapor.

It is difficult to extract sodium from salt, and although salt is the cheapest sodium compound, the sodium of the world (about 5000 tons per year) is made from *caustic soda* by a method we shall study later. Sodium is used in the preparation of dyes and other complex carbon compounds and especially in the manufacture of **sodium cyanide,** $NaCN$. Like potassium cyanide, KCN, sodium cyanide is a white poisonous solid, very soluble in water. The solution dissolves gold and is largely used in the cyanide process (p. 29).

291. Action of the Electric Current on Salt Water.—To extract the other element of salt, we shall be obliged to resort to the use of the electric current. A solution of one part of salt in ten of water is placed in the apparatus indicated in Fig. 75. The middle tube serves simply as a funnel to fill the apparatus. Short pieces of platinum wire passing through the glass carry the current to bits of platinum foil, through which it enters and leaves the liquid. These pieces of foil are called the **electrodes.** The foil at which the current enters is the positive (+) electrode or **anode**, and the foil where the current leaves the liquid is the negative (—) electrode or **cathode.** The *direct* current of a dynamo is the most convenient source of current, but an incandescent lamp must be placed in the circuit to increase the resistance. Apparatus in which carbon rods take the place of the platinum foil is often used in this experiment, since the platinum may be damaged.

The colorless gas which appears at the cathode proves, when we apply a flame, to be *hydrogen.* It has nothing to do with the salt, but arises from the water by a decomposition which does not interest us at present.

The gas which collects at the anode is yellow-green and suffocating. It does not take fire from a flame. A piece of moist litmus paper held in it is *bleached.* This gas is **chlorine,** the second element of salt. It collects more slowly than the hydrogen because it is more soluble and much of it is absorbed by the water.

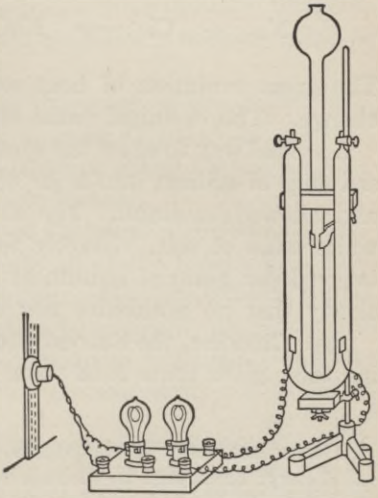


FIG. 75.—Action of the electric current on salt water.

292. **Synthesis of Salt.**—To complete our knowledge of the chemical nature of salt, we must show that it contains no third element. The simplest proof of this is the *synthesis* of salt from sodium and chlorine.

Chlorine, generated in a flask, is passed over a bit of sodium in a bulb, which is warmed with a Bunsen flame. The sodium burns with a dazzling yellow light. When cold, the bulb can be broken, and will be found to contain a white powder, which can be identified by tasting as *salt.*

The black substance which coats the interior of the bulb is the element *silicon,* due to the reducing action of the sodium upon the glass.

Quantitative work shows that salt contains one atomic weight of each of its elements. The symbol of chlorine is Cl and the equation for the synthesis of salt is:

$$\text{Na} + \text{Cl} \longrightarrow \text{NaCl} + 98{,}000 \text{ cal.}$$

The great evolution of heat explains the violence of the change. The chemical name of salt is *sodium chloride.*

A second way to effect the synthesis of salt is to throw thin shavings of sodium into a jar of chlorine, which is covered and allowed to stand. The sodium slowly passes into a white mass of salt. Exactly the same amount of heat is evolved per gram of sodium as in the first method, but so slowly that no noticeable rise in temperature results.

293. Chlorine, the Second Element of Salt.—The following table gives some data about chlorine.

1 **Occurrence:** only in compounds. Salt is the most abundant.
2 **History:** discovered by Scheele in 1774. Davy in 1809 proved it to be an element.
3 **Color:** greenish-yellow.
4 **Odor:** suffocating.
5 **Action on the body:** dangerous irritation of the respiratory passages.
6 **Weight of one liter:** 3.22 grams.
7 **Critical Temperature:** + 146°.
8 **Boiling-point of liquid:** — 34°.
9 **Melting-point of solid:** — 102°.
10 **Solubility:** 100 c.c. water at 20° dissolves 215 c.c.
11 **Chemical character:** intensely active. Even more so than oxygen.
12 **Uses:** chiefly for bleaching paper and cotton; somewhat as a disinfectant.

Since water dissolves more than twice its volume of chlorine, the gas cannot be collected over water. Chlorine is about 2½ times as heavy as air. Hence the tube from the generator can be run into the bottom of an empty bottle. The chlorine collects in the bottom and forces out the air at the top. The color shows when the filling is complete.

The high critical temperature of chlorine indicates that it is easy to liquefy it by pressure alone at ordinary temperatures. Liquid chlorine in steel cylinders is now an article of commerce.

Chlorine is chiefly made by the action of the electric current upon salt-solution. In Germany potassium chloride, KCl, is abundant, and is used instead of salt for the preparation of chlorine by the electric method.

294. Chemical Properties of Chlorine.—Chlorine, in presence of water vapor, converts all of the metals into their chlorides. With the more active metals, like sodium, copper and iron, the union is rapid and the temperature may rise high enough to make the products luminous.. Inactive metals, like gold and platinum, combine slowly with chlorine.

Most of these combinations fail to occur if the chlorine is carefully dried. Thus sodium remains bright in dry chlorine for years, but if a trace of water vapor is admitted, the formation of salt begins at once and is soon complete. The reason that liquid chlorine can be kept in metal cylinders is that the water is removed during the liquefaction.

Chlorine combines with some of the non-metallic elements, but there are others like nitrogen, carbon and oxygen which are not affected by it. Chlorides of these elements can be made by indirect methods. It is hardly necessary to add that there are no chlorides of the inert elements of the argon group.

Related Topics

295. Distinctions Between Suspensions and Solutions of Solids.—The statements in the following table apply not only to water, but also to other liquids. The freezing-points and boiling-points in (6) and (7) must be those of the liquid under consideration.

	Suspension	*Solution*
1 **Formation**	Made by some external action, such as shaking the solid with the liquid.	Hastened by shaking, but also formed *spontaneously* from solid and liquid in contact.
2 **Appearance**	Turbid	Clear
3 **"Keeping" qualities**	Solid separates	Permanent
4 **Effect of filtering**	Solid retained by filter	Unchanged
5 **Quantity of solid taken up by 100 c. c. of water**	No definite limit	Definite amount at each temperature
6 **Freezing-point**	0°, same as pure water	Always below 0°
7 **Boiling-point**	100° same as pure water	Always above 100°

296. Solutions may be Solid, Liquid, or Gaseous.—There is no reason for restricting solution to liquids. Many alloys (p. 35) are **solid solutions** of the metals they contain. Rubber absorbs large quantities of oxygen, carbon dioxide and other gases forming solid solutions. Many kinds of candy are made by melting the sugar, adding the other ingredients and letting the mass cool to a solid solution without any separation. Glass is another familiar solid solution. Air is an example of a *gaseous* solution. A solution is best defined as a *homogeneous mixture of two or more substances* and it may be liquid, solid, or gaseous. But liquid solutions are easiest to make and handle and are by far the most important.

Definitions

Solution. A uniform mixture of the molecules of two substances.

Soluble. Capable of entering into solution in a given liquid.

Insoluble. The negative corresponding to soluble.

"*Curve.*" A line representing the solubility of a substance in water at different temperatures. This method of plotting results is widely used in science.

Saturated solution. A solution which has been shaken with a solid until the solid ceases to dissolve because its concentration has reached the limiting value.

Supersaturated solution. A solution saturated at a higher temperature and then cooled without the separation of any of the solid. A solution which, when brought into contact with the solid which has been dissolved in it, deposits crystals.

Flame test. The identification of a metal by means of the color which its compounds give to the Bunsen flame.

Electrode. A piece of metal, or other conductor, through which the electric current *enters* or *leaves* a solution.

Anode. The conductor through which the electric current *enters* a solution; the *positive electrode.*

Cathode. The conductor through which the current *leaves* a solution; the *negative electrode.*

Direct current. An electric current which flows continuously in the same direction. An *alternating current* flows back and forth, changing its direction many times per second.

Suspension. A turbid mixture of two substances, usually a solid and a liquid.

CHAPTER XVII

HYDROCHLORIC ACID

297. Combustion of Hydrogen in Chlorine.—When a jet from which hydrogen is burning is lowered into a jar of chlorine, the flame becomes large and pale. After the experiment, the gas in the jar is colorless and has a sharp caustic odor, different from that of chlorine, and far less distressing. Blue litmus paper placed in it is not bleached, but reddened. This gas can be nothing but a compound of hydrogen and chlorine. For this reason it is called **hydrogen chloride.**

298. Quantitative Experiment.—The tube in Fig. 76 has a stopcock which divides it into two portions, one of which is just twice as long as the other. The short section is filled with chlorine and the long one with hydrogen. Then the stopcock is opened and the tube allowed to stand in a well-lighted place.

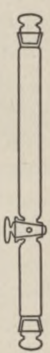


Fig. 76.—The synthesis of hydrogen chloride.

Under the influence of light the two gases slowly unite and since the color of the chlorine completely disappears, we conclude that it has all combined with hydrogen. One end of the apparatus is now placed under mercury and the glass stopper at that end removed. No gas escapes nor does any mercury enter. This proves that the two gases combined without any change in volume, that is, the volume of the hydrochloric acid is simply the sum of the volumes of hydrogen and chlorine which have united to form it.

The stopper is now re-inserted and the tube placed vertically in a vessel of water, with the long section up. Hydrogen chloride, although insoluble in mercury, is very soluble in water, and, when the stopper at the lower end is withdrawn, the water rises until the space left unfilled by it is equal to the volume of the short section of the tube. The gas which remains proves, upon the application of a flame, to be *hydrogen.* Since we started with 2 volumes of hydrogen and 1 volume of chlorine, and since one volume of hydrogen remains unused, it follows that:

1 volume of hydrogen + 1 volume of chlorine ⟶ 2 volumes of hydrogen chloride.

Or,

1 mole of hydrogen + 1 mole of chlorine ⟶ 2 moles of hydrogen chloride

22.4 liters 22.4 liters 44.8 liters

We have seen that the mole of hydrogen contains two chemical unit weights and that the formula of the gas is H_2. The same is true of chlorine. Its formula is Cl_2 (sec. 208).

Hence the equation is:

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

From the molecular point of view, the argument is as follows: According to Avogadro's hypothesis, the statement that

1 volume of hydrogen + 1 volume of chlorine ⟶ 2 volumes of hydrogen chloride

means that

1 molecule of hydrogen + 1 molecule of chlorine ⟵ 2 molecules of hydrogen chloride.

Every molecule of hydrogen separates into two atoms, each of which takes a chlorine atom as a partner and forms with it a molecule of hydrogen chloride. Every molecule of chlorine separates into two atoms, each of which unites with a hydrogen atom:

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

299. Behavior of a Mixture of Equal Volumes of Hydrogen and Chlorine.—The behavior of a mixture of equal volumes of hydrogen and chlorine, under varying illumination, is stated in the following table:

1 *Complete darkness.*	No combination.
2 *Ordinary daylight.*	Slow combination with a speed proportional to the intensity of the light.
3 *Direct sunlight, magnesium light or arc light.*	Instant combination with explosion, but this does not occur if the mixture is absolutely dry or very cold.
4 *Direct application of flame or electric spark.*	Explosion, less violent than in (3).
5 *Thermochemical equation*	$H_2 + Cl_2 \longrightarrow 2HCl. + 52{,}000$ cal.

The attention of the student is called to the interesting influence of light in (1), (2) and (3). He should re-read the description of the formation of starch in plants (p. 191). But there are two important distinctions to be noted here:

1. The formation of starch is accomplished chiefly by the rays which most powerfully affect the eye, the yellow and greenish yellow. These rays have little effect upon the production of hydrogen chloride. The blue and violet rays are the most active.

2. In the formation of starch, energy is absorbed from the light, to be used afterward in running the life-processes of plants and animals. But in the formation of hydrogen chloride, energy is given out. The light merely starts the combination just as a spark may start the explosion of gunpowder, without contributing energy worth mentioning.

The student should notice also the catalytic action of water vapor in (3). The great heat value in (5) explains the explosive character of the mixture and also the fact that hydrogen produces a flame when it unites quickly with chlorine. Chlorine, when led into a jar of hydrogen, can also yield a flame very similar to that of hydrogen burning in chlorine.

300. Properties of Hydrogen Chloride.—The most important properties of hydrogen chloride are as follows:

1 **Appearance:** colorless gas.
2 **Weight of 1 liter:** 1.63 grams.
3 **Critical point:** + 52°.
4 **Boiling-point** of liquid: −84°.
5 **Melting-point** of solid: −110°.
6 **Solubility:** 100 c.c. water dissolve 50,000 c.c. at 0°.
7 **Solubility:** 100 c.c. water dissolve 45,000 c.c. at 15°.
8 **Chemical conduct when dry:** inactive.
9 **Chemical conduct in presence of water:** very active acid.

Owing to its high critical point, the gas can be liquefied by pressure alone, but the liquid, on account of its low boiling-point, cannot be kept in open vessels. The *hydrochloric acid* of the laboratory is a saturated water solution, containing about 40% by weight of hydrogen chloride. When the stopper of the laboratory bottle is removed, hydrogen chloride escapes and produces, with the water vapor of the air, a mist of little globules of hydrochloric acid; this causes the *fuming*, which is more noticeable in damp weather.

301. Chemical Behavior of Hydrochloric Acid Solution.— Hydrochloric acid solution is a good conductor of the electric current, has an intensely sour taste and, like all active acids, is poisonous. It reddens blue litmus and rapidly inverts sugar. It does not affect the precious (inactive) metals, like gold and platinum, and has little or no action upon silver, copper and mercury. Most other metals are rapidly dissolved by it. Hydrogen escapes, and the chloride of the metal dissolves and can be obtained by evaporating the liquid:

$$\underset{\text{Zinc}}{Zn} + 2HCl \longrightarrow \underset{\substack{\text{Zinc}\\\text{chloride}}}{ZnCl_2} + H_2.$$

In order to prove the correctness of this equation, one gram of zinc can be dissolved in hydrochloric acid and the zinc chloride evaporated to dryness and weighed. A simple calculation shows that one chemical unit weight (65.5 grams) of zinc combines with two chemical unit weights ($35.5 \times 2 = 71$ grams) of chlorine. Confirmation is obtained by measuring the hydrogen which escapes when a weighed quantity of zinc is dissolved in hydrochloric acid. 65.5 grams of zinc liberate 22.4 liters of dry hydrogen at S.T.P., which is one mole or two chemical unit weights of hydrogen (2.016 grams).

Magnesium behaves in the same way:

$$Mg + 2HCl \longrightarrow \underset{\substack{\text{Magnesium}\\\text{chloride}}}{MgCl_2} + H_2$$

When a bit of sodium is thrown into concentrated hydrochloric acid, the metal melts to a sphere and runs about, hissing, on the surface. The hydrogen can be lighted with a flame. A white powder made up of little cubes of salt falls to the bottom.

$$Na + HCl \longrightarrow NaCl + H.$$

These cases are quite different from the simple *dissolving* of solids studied in the last chapter. When sugar dissolves in water the principle change is that the molecules of the sugar become widely separated. The state of the sugar is much the same as if it had been changed to a gas, occupying the same volume as the solution, and when the volume is sufficiently reduced by evaporation, sugar separates, just as a gas below its critical temperature condenses to a liquid when its volume is sufficiently reduced by pressure.

But when zinc is placed in hydrochloric acid, it is not really the *zinc* which dissolves. The metal is changed into *zinc chloride*, which dissolves, and *zinc chloride*, not the original zinc, is obtained by evaporation.

Perfectly dry hydrogen chloride, whether liquid or gas, fails to redden blue litmus and has no action on the metals. The same inactivity is noticed when the gas is dissolved in some liquid other than water, like chloroform, benzene or toluene. This striking difference in activity between the dry substance and its water solution has been found also in many other cases. The explanation comes later (Chap. XX).

302. The Deacon Process.—When hydrogen chloride is heated with oxygen (air) chlorine is liberated:

$$2\,HCl + O \rightleftarrows H_2O + Cl_2.$$

The interaction is slow, but in presence of cupric chloride ($CuCl_2$) it becomes rapid enough to serve as the basis of a practical method of making chlorine, called the *Deacon process.* Bits of brick which have been dipped in cupric chloride solution and dried are placed in a little tower and a mixture of hydrochloric acid and air is heated to 400° and passed through them. Since equilibrium results when 80% of the hydrogen chloride is used up, the liberation of the chlorine is incomplete—another instance of the influence of concentration.

The reaction of the Deacon process is reversed when a solution of chlorine in water is exposed to sunlight. Oxygen escapes and hydrogen chloride dissolves:

$$H_2O + Cl_2 \longrightarrow 2HCl + O.$$

303. Laboratory Method of Making Chlorine.—The liberation of chlorine by oxidizing the hydrogen of hydrogen chloride to water is the basis of the method of making chlorine given in the laboratory studies. Hydrochloric acid solution is allowed to drop upon potassium permanganate, $KMnO_4$, which is gently heated:

$$KMnO_4 + 8HCl \longrightarrow KCl + MnCl_2 + 4H_2O + 5Cl.$$

Pyrolusite liberates chlorine in the same way:

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2\,H_2O + Cl_2.$$

It was by this last interaction that Scheele obtained chlorine in 1774. This method is no longer used in the laboratory.

304. Action of Hydrochloric Acid on Oxides and Sulphides.—When zinc *oxide* dissolves in hydrochloric acid no gas escapes, because the hydrogen of the acid forms water with the oxygen of the oxide:

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O.$$

Many other oxides act similarly:

$$\underset{\text{Mercuric oxide}}{HgO} + 2HCl \longrightarrow HgCl_2 + H_2O.$$

$$\underset{\text{Magnesium oxide}}{MgO} + 2HCl \longrightarrow MgCl_2 + H_2O.$$

So far as the formation of the chlorides goes, these equations may be proved in the laboratory. To prove the production of water, dry hydrogen chloride may be passed over the dry oxide which is gently heated. The metallic chloride remains, while drops of water condense in the cooler part of the tube. Why are experiments with hydrogen chloride *solution* valueless as proofs of the formation of water in these interactions?

Hydrochloric acid has little or no action upon the sulphides of mercury, copper and the precious metals. Upon many other sulphides it acts in the same way as upon the corresponding oxides:

$$\underset{\text{Zinc blende}}{ZnS} + 2HCl \longrightarrow ZnCl_2 + H_2S$$

$$\underset{\substack{\text{Iron}\\\text{mono-sulphide}}}{FeS} + 2HCl \longrightarrow \underset{\substack{\text{Ferrous}\\\text{chloride}}}{FeCl_2} + H_2S$$

The second interaction is the basis of the laboratory method of making hydrogen sulphide.

305. Decomposition of Hydrochloric Acid by Heat and by the Electric Current.—Compounds which are formed from their elements with much evolution of heat are *stable*. Hydrogen chloride is an instance. At 1800°, which is far beyond a white heat, the gas begins to decompose.

When the electric current passes through hydrochloric acid solution, hydrogen escapes at the negative pole and chlorine at the positive. The apparatus is the same as that employed in decomposing salt (Fig. 75). Since some chlorine dissolves in the water, the volume of chlorine is smaller than that of hydrogen, especially at first. Later, when the water becomes saturated with chlorine, there is an approach to the equality of volumes which the equation demands:

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

A reference to sec. 299 will show that 52,000 cal. must be *absorbed* in this process. Hence the need for a *continuous supply of energy* in the form of the electric current. The decomposition ceases instantly when the current is interrupted.

Dry hydrogen chloride (liquid or gas) is a non-conductor. So, also, are solutions of it in liquids like chloroform, benzene and toluene. The student should notice that *those forms of hydrogen chloride which are chemically inactive are also non-conductors.* The explanation of this striking fact will be given in Chap. XX.

306. Action of Sulphuric Acid on Salt.—When strong sulphuric acid, H_2SO_4, is poured over salt, a violent escape of hydrogen chloride occurs, and *sodium hydrogen sulphate,* $NaHSO_4$, remains:

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

On the contrary, when hydrochloric acid is added to a solution of sodium hydrogen sulphate, sulphuric acid is formed and a powder composed of little cubes of salt falls to the bottom:

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

Concentration always supplies an easy explanation of such cases. When sulphuric acid is poured over salt, the hydrogen chloride escapes and its concentration in the liquid is kept low. This prevents any interaction between it and the sodium hydrogen sulphate formed.

Salt is nearly insoluble in concentrated hydrochloric acid. Hence, when the latter is added to sodium hydrogen sulphate solution, the salt separates in crystals, and its concentration in the liquid can not rise much above zero. Therefore the inter-action between the salt and the sulphuric acid can not progress.

These experiments prove nothing regarding the *relative activities* of the two acids. That hydrochloric acid is *more active* than sulphuric is shown by other methods, for instance by the fact that, under the same circumstances, it inverts sugar more rapidly

Hydrochloric acid is made on a large scale by the interaction of sulphuric acid and salt in iron pans. The gas is dissolved by passing it through large stoneware bottles containing water. Or, it is passed in at the bottom of a tower packed with coke over which water trickles.

CHAPTER XVIII

VALENCE.—DETERMINATION OF ATOMIC WEIGHTS

307. Valence.—Following are the formulas of some hydrogen compounds:

I	II	III	IV
Hydrochloric acid	Water	Ammonia	Methane
HCl	H_2O	NH_3	CH_4
	Hydrogen Sulphide		
	H_2S		

An atom of chlorine is able to hold one atom of hydrogen in combination to form a molecule. But an atom of oxygen holds two hydrogen atoms; an atom of nitrogen, three; and an atom of carbon, four. This has nothing to do with the *energy* with which the elements unite. Chlorine unites violently with hydrogen while carbon does so with great difficulty; yet the combining power of carbon is four times as great as that of chlorine.

To the combining power of the atoms the name **valence** has been given:

Chlorine in *hydrogen chloride*, HCl, has a valence of 1, or is *univalent*,
Oxygen in *water*, H_2O, " " " 2, " *bivalent*,
Nitrogen in *ammonia*, NH_3, " " " 3, " *trivalent*,
Carbon in *methane*, CH_4, " " " 4, " *quadrivalent*

We are not obliged to connect the notion of valence with the idea of *atoms*. There are always two ways of stating a thing of this kind. We can just as well say that an atomic weight of chlorine (35.5 grams) is able to hold one atomic weight of hydrogen (1.008 gram), while an atomic weight of oxygen (16 grams) holds two, an atomic weight of nitrogen (14 grams) three, and an atomic weight of carbon (12 grams) holds four atomic weights of hydrogen.

308. Determination of Valence.—Since about two-thirds of the elements, including most of the metals, seem to form no hydrogen compounds, their valence must be determined from their compounds with other elements. Thus, chlorine combines with hydrogen atom to atom, and we conclude that, the combining power of the chlorine atom is equal to that of the hydrogen atom. This being the case, we can determine the valence of elements from the formulas of the chlorides.

Zinc forms no hydrogen compound, but it forms a chloride, $ZnCl_2$. Zinc, then, is *bivalent*. This conclusion is confirmed by the study of other zinc compounds, for example:

Hydrogen Compound	*Zinc Compound*
Water, H_2O	Zinc Oxide, ZnO
Hydrogen sulphide, H_2S	Zinc sulphide, ZnS
Sulphuric acid, H_2SO_4	Zinc sulphate, $ZnSO_4$
Nitric acid, HNO_3	Zinc nitrate $Zn(NO_3)_2$

In each case the zinc atom takes the place of two hydrogen atoms. This at once relieves the student of the labor of memorizing the formulas of the zinc compounds.

From the formula of salt, NaCl, it seems that sodium is univalent. We can at once write the formulas of the four sodium compounds corresponding to the hydrogen compounds in the above list, by simply substituting Na for each H.

Sodium oxide	Na_2O
Sodium sulphide	Na_2S
Sodium sulphate	Na_2SO_4
Sodium nitrate	$NaNO_3$

What will be the formulas of the corresponding compounds of a *trivalent* metal, e. g. aluminium?

309. **The Value of Valence.**—Valence is not a fact. It is an attempt to arrange the facts of our science according to the idea of combining power, just as books are classified in a library according to subjects. Its chief value is to assist the student in becoming familiar with the formulas of the compounds. It works well with some elements and badly with others. Thus zinc is always bivalent and, if the student grasps the meaning of this, he need pay no attention to the formulas of the zinc compounds, for he can write them for himself. Carbon is almost always quadrivalent and this is of great assistance in studying the countless compounds of the element. Silver is practically always univalent, so the formulas of its compounds are like those of the corresponding compounds of hydrogen or of sodium.

But to perceive that the method does not always work so smoothly, we need only look at the formulas of three sulphur compounds:

1. Hydrogen sulphide H_2S,
2. Sulphur dioxide SO_2,
3. Sulphur trioxide SO_3.

In (1) the sulphur is bivalent. Since oxygen is bivalent also, we might expect the two elements to unite atom to atom, but no such compound is known. Instead, we find that sulphur is quadrivalent in (2), while in (3) it has a valence of six. As these instances show, the notion of valence is of little use in dealing with the sulphur compounds. We are obliged to study each compound separately, without the help of any general principle. As a rule, however, it pays to remember the valence of an element in studying its compounds. The exceptions can be noted as they occur and they are usually not numerous enough to cause much trouble. In the table in the appendix the valences of some of the common elements are given.

310. Illustration of the Way Atomic Weights are Determined.—On pages 84 to 88 the method of determining atomic weights is taken up, using the oxides and sulphides as a basis. These pages should be re-read.

Let us choose mercury as an example and start by assuming that we know nothing about the atomic weight of the element or the formulas of its compounds. A weighed quantity of mercuric oxide is heated and all the mercury given off is collected and weighed. The result shows that the standard quantity of oxygen (16 grams) combines with 200 grams of mercury. The method is so exact that the error in the final result could hardly amount to 0.001 gram of mercury.

We do not know the formula of mercuric oxide. If it is HgO, our result shows that the atomic weight of mercury is 200. But suppose the formula is Hg_2O. Then the 200 grams of mercury we have obtained are two atomic weights, and the atomic weight is $\frac{200}{2} = 100$. On the other hand, if the formula of mercuric oxide is HgO_2 then the 200 grams of mercury which we have proved to combine with 16 grams of oxygen is only half of an atomic weight of mercury and the atomic weight is $200 \times 2 = 400$ grams. The analysis of mercuric oxide shows us that the atomic weight of mercury is 200 or some multiple or fraction of 200, but it does not show us which multiple or fraction to choose. In fact, until about 1830 the formula of mercuric oxide was taken as HgO_2, and the atomic weight of mercury as 400.

311. Analysis of Mercuric Chloride.—Now let us analyze *mercuric chloride.* A weighed quantity is heated with powdered lime, which combines with the chlorine. The mercury which vaporizes is collected and weighed. The result shows that the atomic weight of chlorine (35.5 grams) is combined with 100 grams of mercury. Again we are confronted with the same doubt. If the formula of mercuric chloride is $HgCl$, the atomic weight of mercury is 100; the formula $HgCl_2$ gives 200 and $HgCl_4$, 400. Since chlorine is univalent in its compounds with the metals, we do not need to consider the possibility of several atomic weights of mercury uniting with one of chlorine.

312. The Mole of Mercuric Chloride.—The doubt can be settled by ascertaining the mole (molecular weight) of mercuric chloride. The mole is the weight of 22.4 liters of the vapor at S.T.P., that is, the weight of the vapor required to fill our standard cube (p. 110).

Mercuric chloride is a solid at S.T.P. and we must weigh the vapor at a higher temperature, say 546°. This is $546° + 273° = 819°$ absolute temperature.

546° is chosen to simplify the calculation. Any temperature above 300° (the boiling-point of mercuric chloride) can be used.

Since the volume of a mass of gas is proportional to its absolute temperature, the standard volume occupied by the moles of all gases at S.T.P., 22.4 liters, becomes at 819° absolute:

$$22.4 \times \frac{819}{273} = 22.4 \times 3 = 67.2 \text{ liters.}$$

The result shows that the weight of 67.2 liters of mercuric chloride vapor at 546° is 271 grams.

The standard cube (22.4 liters) which holds the mole (molecular weight) of all gases would hold 271 grams of mercuric chloride vapor, if the latter could exist at S.T.P. Of this quantity, our analysis shows that 200 grams must be mercury and 71 grams chlorine. Two conclusions follow:

1. Mercuric chloride contains two atomic weights of chlorine. Its formula is not $HgCl$ or $HgCl_4$. *Very likely* it is $HgCl_2$.

2. The atomic weight of mercury is not greater than 200. The fact that we have found 200 parts of mercury in the mole of one compound at once fixes 200 as the highest possible value. But so far we have no proof that the atomic weight is not a fraction of 200, 100 for example. We have seen that this would make the formula of mercuric oxide Hg_2O. In the same way, that of mercuric chloride would be Hg_2Cl_2, for the 200 grams of mercury in the mole would be two atomic weights. The mole would still be 271.

313. The Mole of Mercury.—How, then, do we know that 200, not 100, is the correct value? This question is answered by a wider study of the compounds of mercury. Many of them have been vaporized and the weight of a liter of the vapor ascertained. From this the weight of the vapor which would fill the standard cube of 22.4 liters at S.T.P. has been calculated. This fixes the value of the mole (molecular weight). Now, in the mole of all these compounds, we always find 200 grams of mercury or some small multiple, never less than 200. Hence 200 grams—not 100—is the true atomic weight. We must recall also the fact that for the vapor of mercury itself, the mole is 200 (p. 160).

314. The Law of Dulong and Petit.—Further aid comes from another quarter. About a century ago two French chemists, *Dulong* and *Petit*, determined the *specific heats* (p. 36) of a number of the elements. From these they calculated the amount of heat required to warm the atomic weight through 1°. Thus it requires 0.112 calorie to warm one gram of iron through 1°. Since the atomic weight of iron is 56, it will take $0.112 \times 56 = 6.3$ cal. to warm the atomic weight of iron 1°.

Now it happens that the atomic weight of cadmium (112) is twice that of iron. The specific heat of cadmium, determined by experiment, turns out to be 0.056, which is just half that of iron. Hence the amount of heat required to warm the atomic weight of cadmium 1° is 0.056 × 112 = 6.3 cal., which is identical with the result obtained for iron. That this is not a mere accident is plain when the same calculation is made for other elements:

Name	*Specific Heat*	*Atomic Weight*	*Product*
Sodium	0.29	23	6.6
Zinc	0.096	65.5	6.3
Lead	0.031	207	6.4
Mercury	0.032	200	6.4
Gold	0.032	197	6.3
Silver	0.057	108	6.2

It is clear that the amount of heat required to warm the atomic weight of these elements through 1° is nearly the same for all, amounting to about 6.4 cal. We have

$$\text{Specific heat} \times \text{atomic weight} = 6.4, \text{ or}$$

$$\text{atomic weight} = \frac{6.4}{\text{specific heat}}$$

Thus the analysis of mercuric oxide and of mercuric chloride shows that the atomic weight of mercury is some multiple or fraction of 200. The specific heat of mercury is 0.032.

$$\text{Atomic weight} = \frac{6.4}{0.032} = 200,$$

which shows at once that 200 *is the correct atomic weight.*

From the variation in the numbers under "product" in the table, it appears that the law of Dulong and Petit is not very exact. This does not interfere with its use. The atomic weight is really calculated from the chemical analysis, which can be made as accurate as we please. The object of the law of Dulong and Petit is merely to point out which multiple to select. Thus, it indicates that the atomic weight of mercury cannot be 100 or 400, but must be very close to 200, and this is all that is required of it, for the exact value of the atomic weight can then be calculated from the chemical analysis.

Related Topics

315. The Atomic Weight of Sulphur.—The methods which may be employed in determing the atomic weight of sulphur are good illustrations of the important principles we are now studying.

On p. 94 we have discussed a method by which a weighed quantity of sulphur can be burned, and the sulphur dioxide weighed. We find that the weights of the two elements which combine are equal, so that 16 grams of oxygen would unite with 16 grams of sulphur. It follows that the atomic weight of sulphur is some multiple or fraction of 16.

For some reason as yet unexplained, the law of Dulong and Petit does not work as well with the non-metals as with the metals. The specific heat of sulphur is 0.18.

$0.18 \times 16 = 2.9$ cal., which is far below the usual value of about 6 cal.

$0.18 \times 32 = 5.8$, which is close enough to indicate that 32 is the correct figure.

We have seen that the atomic weight of mercury is 200. Assume that the formula of cinnabar, mercuric sulphide, is HgS. Then the atomic weight of sulphur will be simply that quantity which unites with 200 grams of mercury. The composition of cinnabar is:

Mercury	86.21%
Sulphur	13.79%

$$86.21 : 13.79 :: 200 : x$$

From which $x = 32$ for the atomic weight of sulphur. On p. 86 we applied a similar proportion to the composition of lead sulphide with the same result.

A weighed quantity of silver powder can be changed, by heating in sulphur vapor, to silver sulphide (Ag_2S), which is weighed. The result for the composition of silver sulphide is:

Silver	87.10%
Sulphur	12.90%

If silver sulphide contains two atomic weights of silver ($Ag = 108$) our proportion becomes

$$87.10 : 12.90 :: 216 : x \ldots x = 32.$$

These experiments are very exact and they show that the atomic weight must be 32 or some multiple or fraction of 32. They do not tell us which multiple to choose, for we have taken the formulas of the sulphides for granted. So far the only fact bearing upon this point is the specific heat, and that gives a doubtful answer. Just as with mercury, the question is answered by determining the mole (molecular weight) of a number of gaseous sulphur compounds.

Name	*Weight of 22.4 liters of gas or vapor calculated to S.T.P.*	*Sulphur in 22.4 liters*
Sulphur dioxide	64 grams	32 grams
Sulphur trioxide	80 grams	32 grams
Hydrogen sulphide	34.016 grams	32 grams
Carbon disulphide	76 grams	64 grams
Sulphur chloride	135 grams	64 grams

In the second column are the weights of the gases or vapors required to fill the standard cube of 22.4 liters at S.T.P., while the third column gives the sulphur contained in those weights. Since no sulphur compound contains less than 32 grams of sulphur in 22.4 liters of its vapor, 32 is taken as the correct value for the atomic weight. Carbon disulphide, CS_2, and sulphur chloride, S_2Cl_2, contain two atomic weights of sulphur.

Oxygen is taken as the **basis** of the table of atomic weights because oxygen forms compounds with nearly all the other elements, and the atomic weights, as we have seen, are often determined by analyzing the oxides. The choice of **16** parts of oxygen by weight as a standard is purely a matter of convenience. If a smaller quantity than 16 parts was taken, elements like nitrogen, lithium and hydrogen—whose atomic weights, under the present system, are less than 16—would have fractional atomic weights. Another advantage of 16 parts of oxygen by weight as a standard is that the atomic weight of *hydrogen* is close to unity, so close that, in rough calculations, it can be taken as unity without serious error.

Definitions

Valence. The combining power of the atom of an element. The valence of an atom is measured by the number of hydrogen atoms it is able to hold in combination.

Univalent. Having the same combining power as hydrogen.

Bivalent. Having twice the combining power of hydrogen.

Trivalent. Having three times the combining power of hydrogen.

Quadrivalent. Having four times the combining power of hydrogen.

CHAPTER XIX

IMPORTANT COMPOUNDS OF CHLORINE WITH THE ELEMENTS ALREADY STUDIED

316. Chlorides of the Metals.—The following table contains some information about the compounds of chlorine with some of the metals. Notice the very small solubility of silver chloride (1), equalling one part in 625,000 parts of water. Mercurous chloride dissolves to about the

Properties of Some Metallic Chlorides

Name	*Formula*	*Description*	*Melting Point*	*Boiling Point*	*Grams Dissolved by 100 c.c. Water (18°)*	*Uses*
1 **Silver chloride**	$AgCl$	White curdy	260°	unknown	0.00016	Exists in sensitive layer of photographic paper
2 **Lead chloride**	$PbCl_2$	White needles	447°	900°	1	None
3 **Mercurous chloride**	$HgCl_2$	White powder	none	sublimes	0.0002	Medicine
4 **Mercuric chloride**	$HgCl_2$	White crystals	260°	300°	7.4	Dilute solution as disinfectant
5 **Tin dichloride**	$SnCl_2$	White crystals	250°	606°	270	Mordant in dyeing
6 **Zinc chloride**	$ZnCl_2$	White crystals	100°	730°	300	Solution for cleaning metals before soldering, and as an embalming fluid

same extent. Such substances are often said to be "insoluble" in water. Lead chloride is an example of slight solubility, while mercuric chloride is moderately soluble, and zinc chloride very soluble. Mercurous chloride (3) is called "calomel." When heated it *sublimes;* that is, it vaporizes directly from the solid state, without melting. It is a valuable medicine. Mercuric chloride (4) is called "corrosive sublimate." The dilute solution is much used for disinfecting the surface of the body and the surgeon's hands before operation. Mercuric chloride is poisonous. The antidote is white of egg, or large quantities of milk, taken at once.

Especially in dyeing cotton, it is found that many colors are not "fast," that is, they are washed out of the fabric by water. But if the fabric is soaked in a solution of tin dichloride (5) before dyeing, it can then be dyed "fast." The tin compound in the fabric forms an insoluble compound with the dye. Substances which are used to fix dyes in this way are called *mordants.* They are chiefly compounds of tin, aluminium, iron or chromium.

317. Some Non-metal Chlorides.—Since the *non-metals* and their oxides are not affected by hydrochloric acid, their chlorides are made by the direct union of the two elements, or by other special methods.

Sulphur chloride, S_2Cl_2, is made by passing chlorine over hot sulphur. It is a reddish yellow liquid with an unpleasant odor. It dissolves sulphur and is used in vulcanizing rubber.

Chlorine does not combine directly with oxygen or nitrogen. Three compounds with oxygen and two with nitrogen have been prepared indirectly. All five are endothermic and highly explosive. They cannot be used for blasting, because they are so easily exploded by shock that they cannot be transported or handled.

318. Action of Chlorine on Methane.—When a mixture of chlorine with methane is exposed to sunlight, the hydrogen atoms of the methane are replaced by chlorine step by step.

The hydrogen unites with more chlorine, producing hydrogen chloride:

$$CH_4 + Cl_2 \longrightarrow \underset{\substack{\text{Methyl}\\\text{chloride}}}{CH_3Cl} + HCl \quad (1)$$

$$CH_3Cl + Cl_2 \longrightarrow \underset{\substack{\text{Methylene}\\\text{chloride}}}{CH_2Cl_2} + HCl \quad (2)$$

$$CH_2Cl_2 + Cl_2 \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + HCl \quad (3)$$

$$CHCl_3 + Cl_2 \longrightarrow \underset{\substack{\text{Carbon}\\\text{tetra-chloride}}}{CCl_4} + HCl \quad (4)$$

Methyl chloride, CH_3Cl, is a gas, which is compressed to a liquid and sold in cylinders. It is used in the manufacture of dyes.

Chloroform, $CHCl_3$, is a heavy liquid with a pleasant odor. It is used as an anæsthetic.

Carbon tetra-chloride, CCl_4, is a colorless liquid (specific gravity 1.6). It is used in cleansing and scouring as a substitute for gasoline, over which it has the great advantage of not being inflammable. Since it contains no hydrogen, chlorine has no action upon it.

Chlorine acts in the same way upon other hydrocarbons. The compounds produced are called *substitution products*, because the chlorine takes the place of the hydrogen. Other non-metallic elements, like bromine (Chap. XXI) act in the same way. Since there are many hydrocarbons, and since substitution can take place in many ways, the total number of substitution products is very great. They can be prepared not only from the hydrocarbons, but also from other carbon compounds. Thus methyl chloride, chloroform and carbon tetra-chloride are not made practically from methane but by other methods which, at present, are cheaper and more convenient for production on a large scale. However, the invention of a suitable process is all that is needed to make it very profitable to manufacture these substances from methane. *Natural gas* would be a suitable raw material.

319. Sal-ammoniac.—*Sal-ammoniac* is a mineral which is found as a white crust on lavas about Aetna, Vesuvius and other volcanoes. It occurs sparingly, but is made artificially in large quantities, for it has important applications. Its use in filling batteries for door-bells and explosion-engines is familiar to the student. Some of the facts concerning sal-ammoniac are summarized below:

Appearance: small, white crystals.
Taste: sharp, salty.
Specific gravity: 1.5.
Behavior when heated: vaporizes without melting (see below).
Solubility: 100 c.c. water dissolves 37 grams at 20°, more at higher temperatures. It dissolves with marked absorption of heat. The solution has no effect on the color of red or blue litmus.
Uses: filling electric batteries; frequent ingredient in cough-mixtures and cough-lozenges.

320. Chemical Nature of Sal-ammoniac.—No doubt the student is aware of the fact that the sal-ammoniac in the battery which rings the door-bell becomes exhausted and must be renewed from time to time. He must have noticed also that the zinc rods which dip into the liquid become corroded. It follows that zinc and sal-ammoniac interact, but that the change is very slow. Like all chemical changes, it is greatly quickened when the temperature is raised.

Fig. 77.—Synthesis of sal-ammoniac.

When a mixture of sal-ammoniac and zinc powder is heated in a test tube, ammonia escapes and can be recognized by its odor. That something else is liberated in addition to the ammonia can be shown by collecting the gas over water in the usual way. The ammonia is completely absorbed by the water, but a colorless gas collects, which proves, upon the application of flame, to be hydrogen. The residue in the test tube in which the mixture was heated contains zinc chloride, $ZnCl_2$.

This experiment proves that sal-ammoniac contains nitrogen, hydrogen and chlorine. Quantitative information can be obtained by the synthesis of sal-ammoniac from ammonia and hydrogen chloride (Fig. 77). 10 c.c. of ammonia gas and 10 c.c. of hydrogen chloride are collected in small measuring cylinders over mercury. The hydrogen chloride is then allowed to pass up without loss through the mercury into the ammonia. A white smoke is formed and the mercury rises. When the combination is complete, it is found that both gases have disappeared. The white solid in the cylinder proves to be sal-ammoniac.

The two gases have united volume to volume, which means molecule to molecule. The simplest equation, therefore, is:

$$NH_3 + HCl \longrightarrow NH_4Cl.$$

The formula NH_4Cl requires a molecular weight of 53.5. Now, when 53.5 grams of sal-ammoniac is vaporized, the volume of the vapor, calculated to S.T.P., amounts to 44.8 liters instead of the 22.4 we should expect. This caused much discussion among chemists, until it was shown that, when heated, the sal-ammoniac decomposes:

$$NH_4Cl \longrightarrow NH_3 + HCl.$$

Since this doubles the number of molecules present, it doubles the volume of the vapor. As soon as the vapor cools, re-combination to sal-ammoniac takes place, so that careful work is necessary to show that the sal-ammoniac has ever been separated at all.

Decomposition of this sort, caused by heat and reversed by cooling, is very common. It is called *dissociation.*

If the sal-ammoniac is free from every trace of water, it does *not* dissociate when heated. In that case, 53.5 grams of the vapor occupy, calculated to S.T.P., the normal volume of 22.4 liters. It is interesting, also, that perfectly dry ammonia can be mixed with perfectly dry hydrogen chloride without the formation of any sal-ammoniac.

We can now write the equation for the interaction of sal-ammoniac and zinc:

$$Zn + 2\,NH_4Cl \longrightarrow ZnCl_2 + 2\,NH_3 + H_2.$$

321. **Ammonium Compounds.**—Sal-ammoniac is similar to the chlorides described in the table (p. 233). Its resemblance to salt is especially close. Like salt it often crystallizes in cubes, its taste is similar, it is soluble in water to about the same extent, it gives off hydrogen chloride when treated with sulphuric acid, and so on. We should violate all

the principles of good classification if we refused to call sal-ammoniac a *chloride.*

A glance at the three formulas:

$$HCl \qquad NaCl \qquad NH_4Cl$$

shows that the part of the atom of hydrogen in hydrochloric acid, and of the atom of sodium in table-salt, is played, in sal-ammoniac, by a *group of five atoms,* NH_4. A molecule of sal-ammoniac is composed of this group, united to an atom of chlorine.

To the group NH_4 the name **ammonium** is given. The chemical name, then, of sal-ammoniac is **ammonium chloride.**

Corresponding to each of the sodium compounds is an ammonium compound, in which the place of the sodium atom is taken by the group NH_4. We may illustrate by the most familiar and important three compounds of both classes:

Acids	*Sodium Compounds*	*Ammonium Compounds*
Hydrogen chloride HCl	Sodium chloride $NaCl$	Ammonium chloride NH_4Cl
Nitric acid HNO_3	Sodium nitrate $NaNO_3$	Ammonium nitrate NH_4NO_3
Sulphuric acid H_2SO_4	Sodium sulphate Na_2SO_4	Ammonium sulphate $(NH_4)_2SO_4$

It will be noted that *ammonium* (NH_4) differs from *ammonia* (NH_3) by one atom of hydrogen. It also differs from ammonia in the important respect that it is *not a real substance.* No one has succeeded in obtaining ammonium by itself. It is merely a group of atoms, which exists in the molecules of a whole series of compounds, but never alone.

Such a group of atoms is called a **radical.** Another example of a radical is *methyl,* CH_3. There are many methyl compounds:

Methyl oxide	$(CH_3)_2O$
Methyl sulphide	$(CH_3)_2S$
Methyl chloride	CH_3Cl
Methyl nitrate	CH_3NO_3
Methyl sulphate	$(CH_3)_2SO_4$

and hundreds of others. Like ammonium, methyl cannot exist by itself. It will be noted that both radicals are univalent.

Related Topics

322. Salts.—Some of the chlorides of the metals are described in the table at the beginning of this chapter. There are many others, for the hydrogen of hydrogen chloride can be replaced by many metals. The metallic chlorides which result are called the *salts* of hydrochloric acid.

In the same way, there corresponds to nitric acid (HNO_3) a series of salts formed by the replacement of its hydrogen by metals. *Sodium nitrate* ($NaNO_3$) is an example. *Sodium sulphate* (Na_2SO_4) is an example of the salts of sulphuric acid (H_2SO_4).

Table-salt, which has been known for ages, was the first "salt," and the term was gradually extended to other substances which seemed to resemble it more or less. The salts are crystalline solids, usually odorless, less easily vaporized and less active chemically than the corresponding acids. Their water solutions conduct the electric current and, *when nothing but water and the salt are present,* do not affect the color of either red or blue litmus. A re-inspection of the table of metallic chlorides (p. 233) will show the great variation in properties among the salts of the same acid.

Compounds in which the hydrogen of acids is replaced by *radicals* are classed as salts when their properties require it, otherwise not. We have just seen that all the properties of *ammonium chloride* stamp it as a salt in which the hydrogen of hydrochloric acid is replaced by ammonium.

In *methyl chloride,* CH_3Cl, the hydrogen of hydrochloric acid is replaced by methyl, CH_3, yet the following statement of its properties will show that it would be absurd to regard it as a salt: It is a gas with an ethereal odor. It does not interact with sulphuric acid. It is slightly soluble in water; the solution has no salty taste and does not conduct the electric current.

For similar reasons, methyl nitrate, CH_3NO_3, and methyl sulphate $(CH_2)_3SO_4$ cannot be regarded as salts of the corresponding acids. Such compounds are put into a class by themselves and are called **esters.**

Non-metallic chlorides, like sulphur chloride and carbon tetrachloride, have none of the properties of salts.

Definitions

Sublime. To vaporize directly from the solid state, without melting.

Mordant. A substance used in dyeing, not as a color, but to make the dye adhere to the fabric.

Dissociation. Decomposition, caused by heat and reversed by cooling.

Radical. A group of atoms found in the molecules of a whole class of compounds.

Salts. Compounds in which the hydrogen of acids is replaced by metals or by radicals.

Esters. Compounds in which the hydrogen of acids is replaced by radicals composed of carbon and hydrogen. Esters differ completely from salts in properties.

CHAPTER XX

SYLVITE, POTASSIUM, CAUSTIC SODA AND CAUSTIC POTASH.—SUGAR SOLUTION COMPARED WITH SALT SOLUTION

323. **Sylvite.**—*Sylvite* is a mineral which is found at **Stassfurt** and elsewhere in northern Germany. Its resemblance to rock-salt is close, as will be seen from the following paragraph and this suggests the probability of a close chemical relationship between the two minerals.

When pure, sylvite forms colorless crystals, not cubical, but readily breaking along the faces of a cube when struck. Its taste is salty and bitter. At room-temperature, its solubility in water is nearly the same as that of table-salt. Cold water dissolves less sylvite than salt and hot water more; that is, its solubility is more influenced by temperature than that of salt. When the electric current is passed through a solution of sylvite, chlorine is set free at the anode and hydrogen (from the water) at the cathode, just as with table-salt. Sylvite is therefore a *chloride.*

In the Bunsen flame, sylvite produces a delicate *violet* color. This flame color is a proof of the presence of a metal called *potassium,* which is very similar to sodium.

324. **Properties of Potassium.**—The following table gives some data concerning potassium:

Appearance: silver-white metal, tarnishes instantly in the air.

Symbol: K (from German "Kalium").

Specific Gravity: 0.86.

Chemical conduct: intensely active, even more so than sodium.

Hardness: softer than sodium, easily cut with a knife.

Atomic weight: 39.

Melting-point: 62°.5.

Boiling-point: 720°: vapor is green and contains only one atom in the molecule.

Uses: none.

325. Synthesis of Sylvite.—In order to show that no third element is present in sylvite, we may burn potassium in chlorine, just as we did sodium (p. 211). There is an energetic combustion, violet light being radiated, instead of yellow. The white substance left in the bulb is identical with powdered sylvite. Sylvite is therefore *potassium chloride.* Quantitative work shows that its formula is KCl. The combination of potassium and chlorine may be written thus:

$$K + Cl \longrightarrow KCl + 106{,}000 \text{ cal.}$$

Although the light display is less dazzling than in the synthesis of table salt, the total energy evolved is greater (p. 212). Nevertheless, a *gram* of sodium burned in chlorine, gives more heat than a gram of potassium. Why?

326. The Stassfurt Salts.—The city of Stassfurt (population 20,000) is in North Germany, forty miles south of Magdeburg. Salt wells have been worked there for centuries and this fact caused the Prussian government to undertake borings which, in 1843, penetrated into a bed of rock-salt more than 1000 meters thick. Above this are layers containing potassium chloride and potassium sulphate with other substances. These upper layers—often 100 meters or more thick—which yielded no sodium chloride, were at first regarded as a mere nuisance. They have proved to be the most valuable portion of the deposit. Millions of tons of more or less impure potassium chloride and potassium sulphate are obtained at Stassfurt yearly, some of which goes into the chemical industries. Most of it, however, is used by farmers as a fertilizer, for potassium compounds are indispensable to the growth of plants.

Similar deposits have been detected by borings made at many other places quite remote from Stassfurt, so that they must exist under great areas of North Germany. Their total value to chemical industry and to agriculture is beyond calculation. Some of the giant sea-weeds which grow along the coast of California contains as much as 35 per cent of their dry weight of potassium chloride. They also contain considerable quantities of iodine.

327. Action of Sodium on Water.—We have seen that sodium liberates hydrogen from hydrochloric acid (p. 219).

One atomic weight of sodium (23 grams) sets free one atomic weight of hydrogen (1.008 grams):

$$Na + HCl \longrightarrow NaCl + H.$$

Sodium also liberates hydrogen violently from water. When the metal is weighed, and the weight of the hydrogen calculated from its volume, it is found that a fixed weight of sodium sets free the same weight of hydrogen from water as from hydrochloric acid. In either case:

$$Na \text{ (23 grams) yields } H \text{ (1.008 gram).}$$

The experiment is always carried out with a large excess of water, so that the small but definite quantity of water which disappears by interacting with the bit of sodium is not missed.

The liquid which remains has acquired a bitter taste and feels soapy between the fingers. It turns red litmus paper *blue*, reversing the color-change produced by acids. The dissolved substance, which is responsible for these new properties, can be obtained by evaporation to dryness, when a white solid remains, which is called *caustic soda* on account of its corrosive action on animal and vegetable tissues and on many metals.

That this caustic soda contains the *sodium* used can be shown by holding a bit of it in the flame, when the strong yellow color betrays the presence of the metal. That it contains *hydrogen* can be proved by heating it with powdered zinc and collecting the gas over water. With a fixed weight of sodium, the weights of hydrogen liberated in the two experiments (1) when the metal is treated directly with water, (2) when the caustic soda is afterward heated with zinc powder, are *exactly the same. Sodium liberates half the hydrogen from water; the other half remains in the caustic soda.*

These results can be summed up in the equation:

$$Na + H_2O \longrightarrow NaOH + H.$$

Caustic soda, $NaOH$, differs from the oxides in containing hydrogen in addition to oxygen. Hence its chemical name, *sodium hydroxide.*

328. Sodium Hydroxide.—*Sodium hydroxide,* NaOH, is often sold for household purposes in cans, under the name "concentrated lye." The purer grades are sold in the form of round sticks which are made by casting the melted substance. It melts below a red heat and is very soluble in water. It must be kept away from air, from which it rapidly absorbs water and carbon dioxide. It is a most important commercial product, being used in great quantities for the manufacture of soap and for other chemical industries.

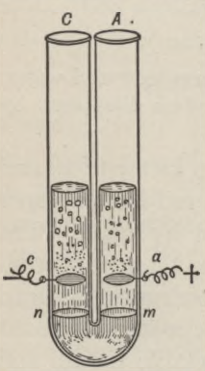


Fig. 78.—Electrolysis of salt solution.

329. Preparation of Sodium Hydroxide.—We are now in a position to understand more fully what happens when the electric current is passed through a solution of salt. Chlorine escapes at the anode and hydrogen from the water at the cathode. Sodium hydroxide is formed at the cathode and dissolves in the water. Using the apparatus of Fig. 75, this fact can be shown by coloring the salt solution with a little red litmus. The litmus will be bleached by the chlorine around the anode, and turned blue at the cathode by the sodium hydroxide. We may assume that sodium separates, for an instant, at the cathode, and at once interacts with the water, liberating hydrogen and forming sodium hydroxide.

Caustic soda is now made very largely by the method indicated above. The chief problem is to keep the chlorine away from the sodium hydroxide, for the two will interact if allowed to come together. In the apparatus of Fig. 78 the layer of mercury *m n* prevents the chlorine liberated at the anode *A* from coming into contact with the sodium hydroxide formed at the cathode *C*. In one form of apparatus, used on a large scale, the vessel is divided into two parts by a porous partition. The anode is in one chamber and the cathode in the other. The chlorine is led away from the anode chamber through a tube, and has no chance to interact with the sodium hydroxide which is formed at the cathode. The partition permits the current to pass because it is porous, and is saturated with salt solution.

Decomposition by the electric current is called **electrolysis.**

330. **Potassium Hydroxide.**—*Potassium* interacts with water in the same way as sodium:

$$K + H_2O \longrightarrow KOH + H.$$

The action is more violent, so that the hydrogen ignites and burns, with a flame colored violet by potassium vapor. Potassium hydroxide is called *caustic potash*. It is very similar to caustic soda, and is made by the same methods, using potassium chloride instead of salt.

331. **Manufacture of Sodium.**—When *melted caustic soda* is electrolyzed, oxygen is liberated at the anode, and sodium and hydrogen at the cathode. Caustic potash behaves in a similar way. It was by this method that *Sir Humphry Davy*, in 1807, discovered sodium and potassium.

$$NaOH \longrightarrow Na + O + H.$$

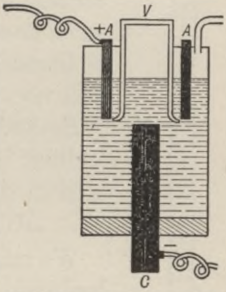


FIG. 79.—Preparation of sodium.

Sodium is now made on a large scale by Davy's process at Niagara and elsewhere. Fig. 79 is a diagram of the apparatus devised by *Costner* for this purpose. The caustic soda is contained in an iron cylinder through the bottom of which the cathode *C* projects. Several anodes *A A* surround the cathode. The sodium collects in a cylindrical vessel *V* which is placed over the cathode. This serves to protect it from the oxygen. The heat produced by the passage of the current keeps the caustic soda melted. It is more difficult to make potassium in this way on account of the tendency of the metal to burn as soon as it is liberated. Since potassium has no important uses, little of it is made.

332. **Bases.**—When hydrogen chloride is passed over a little powdered caustic soda there is an energetic interaction; water is formed and salt remains in the tube:

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

When *solutions* of hydrochloric acid and sodium hydroxide are mixed, the salt remains dissolved and can be obtained by evaporation. The sodium hydroxide can be placed in a dish and colored blue with a drop of litmus. Dilute hydrochloric acid is added from a burette, Fig. 80, which is a graduated tube, with a stopcock at the bottom. The liquid remains blue until all the sodium hydroxide is converted into salt. At this point, a single additional drop of acid turns the liquid red. If it is evaporated, salt is left and can be identified by its taste. As we have seen, salt is far less active than hydrochloric acid or caustic soda, having, for instance, no effect on the color of litmus, little corrosive action on the metals and no caustic action on organic matter.

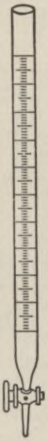


FIG. 80.—A burette.

Potassium hydroxide, which is so similar to sodium hydroxide, interacts with hydrochloric acid in the same way:

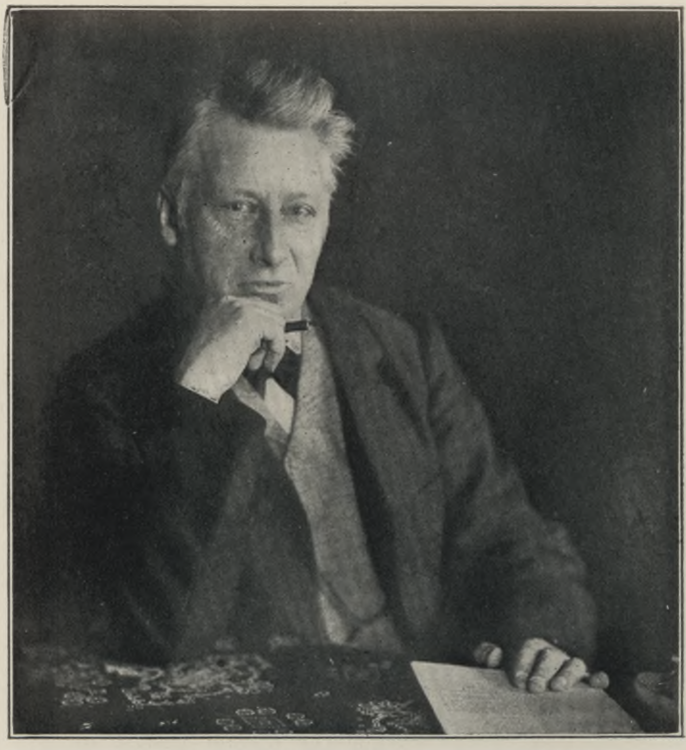
$$KOH + HCl \longrightarrow KCl + H_2O.$$

We may also write the interactions of the two hydroxides with nitric acid:

$$NaOH + HNO_3 \longrightarrow \underset{\text{Sodium nitrate}}{NaNO_3} + H_2O.$$

$$KOH + HNO_3 \longrightarrow \underset{\text{Potassium nitrate}}{KNO_3} + H_2O.$$

The hydroxides of potassium and sodium are types of an important class of substances, the **bases**. A *base* is the hydroxide of a metal. Soluble bases have a *bitter taste,* quite unlike the sour taste of an acid. The *color-changes* produced by acids in sensitive dye-stuffs, like litmus, are *reversed* by bases. Water solutions of bases, like those of acids and salts *conduct the electric current*: solutions of *active* bases and acids conduct *well,* those of *inactive* bases and acids are *poor* conductors. When an acid and a base are brought together, the OH of the base produces water with the H of the acid and the residues of both molecules form a salt. Because the peculiar properties of both acid and base disappear, seeming to destroy each other, the term *neutralization* is applied to the formation of a salt by their interaction.



J. H. VAN'T HOFF

B. Holland, 1852. D. 1911.

Created the modern theory of solutions. Introduced the idea of solid solutions. Investigated the way in which the atoms are arranged in space inside the molecule. Made many experiments on double salts.

Related Topics

333. The Physical Properties of Solutions in Water.—A simple apparatus for finding out whether a water solution conducts the current is shown in Fig. 81. The liquid to be tested is placed in a beaker and the metal electrodes dipped into it. The lamp interposes a resistance which cuts down the current to a suitable strength, and, at the same time, indicates, by lighting up more or less, whether the liquid allows much or little current to pass.

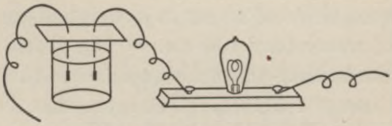


FIG. 81.—Apparatus for testing the conducting power of solutions.

The results show that solutions are of two very different sorts:

1. There is a group which, to all intents and purposes, stops the current altogether, for the lamp fails to light up. To this class belong water solutions of cane sugar, glucose, fruit sugar, glycerine, alcohol, ether, etc.

2. There is another group, the members of which conduct well enough to make the lamp light up more or less brightly. To this class belong water solutions of hydrochloric, nitric and acetic acids, sodium and potassium hydroxides, and salt. In fact, it includes water solutions of all acids, bases and salts. In order to compare results, the solutions should be made so that the strength, measured in moles per liter, is the same for all.

None of these solutions conduct nearly as well as a mass of copper of the same size and shape, but they all conduct much better than pure water. While the current passes, there is evidence of chemical change at the electrodes, escape of gases or separation of metals, as the case may be. That is to say, *electrolysis* is taking place. Hence, the members of this second group are called **electrolytes.** *Acids, bases* and *salts* are electrolytes, other substances are not. The solution of an active acid, like hydrochloric or nitric, allows the lamp to glow brightly, while the solution of an inactive acid, like acetic, shows by the feeble glow of the lamp, that it does not conduct as well. Active and inactive bases show similar differences.

334. The Rise in the Boiling-Point.—We will now leave the electrolytes, to return to them later, and devote ourselves to the *non-conducting solutions*, which are much simpler in their behavior and easier to understand.

A solution of *sugar* boils at a higher temperature than water; the sugar molecules attract the water molecules and make it more difficult for them to leave the liquid and form vapor. There ought, then, to be some connection between the *concentration* of a sugar solution and the temperature at which it boils.

The plain way to get exact information is to dissolve weighed quantities of sugar in a weighed quantity or a measured volume of water (say 100 c.c. = 100 grams) and to measure the rise in the boiling-point with a delicate thermometer, graduated in fractions of a degree. The molecular weight of sugar ($C_{12}H_{22}O_{11}$) is, in round numbers, 342. We cannot well dissolve 342 grams of sugar in 100 grams of water, for the solution would be a thick syrup impossible to work with, but we can use a definite fraction, say one-tenth of the molecular weight (34.2 grams). Dissolving this in 100 c.c. water, we note a rise in the boiling-point of about one-half a degree, from 100° to 100°.5. A second portion of 34.2 grams sends the boiling-point up another half-degree to 101°. Continuing thus with five separate portions of 34.2 grams each, we should observe each time the same rise in the boiling-point. It is really a little more than half of a degree (0.52), so that the liquid after the introduction of the last portion would boil at 102°.6.

The *conclusions* are very definite and simple:

1. The rise in the boiling-point is proportional to the concentration of the solution.

We have used, altogether, half of a molecular weight of sugar (171 grams) and the boiling-point has risen 2°.6. Hence:

2. A molecular weight of sugar dissolved in 100 grams of water causes a rise in the boiling-point of 5°.2.

Now conceive the same experiments repeated with *glucose* ($C_6H_{12}O_6$), the molecular weight of which is, in round numbers, 180. Each portion of 18 grams would raise the boiling-point of 100 grams of water about half a degree (0°.52) so that *a whole molecular weight would raise the boiling-point* 5°.2.

In connection with this it will be interesting to *invert* (p. 195)[1]

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[1] The change of sucrose into grape-sugar and fruit-sugar is called *inversion*.

the cane sugar solution containing 171 grams of sugar in 100 grams of water and study the effect on the boiling-point. From the equation:

$$\underset{\text{Cane Sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fruit sugar}}{C_6H_{12}O_6}$$

it is clear that the inversion will double the number of molecules of dissolved substance. It will also remove nine grams of water (why nine?) which must be replaced before the boiling-point is taken.

Practically, therefore, we add a trace of hydrochloric acid to invert the sugar, nine c.c. of water to replace that used in the inversion and then take the boiling-point. It is now 105°.2. *The inversion has doubled the rise.* Half of a molecular weight of glucose and half of a molecular weight of fruit sugar together raise the boiling-point by the same amount as would a molecular weight of cane sugar, 5°.2. Plainly it is only the *number* of molecules that counts. The kind, size or weight of the molecules has no influence. We now have a basis for a third statement:

3. *A molecular weight of any non-electrolyte, dissolved in* 100 *grams of water, produces a rise in the boiling-point of* 5°.2. Substances, like alcohol, which vaporize with the water, are excluded from this statement. Alcohol *lowers* the boiling-point of water.

335. The Lowering of the Freezing-point.—Sugar solution *freezes* at a *lower* temperature than water. The attraction between the sugar molecules and those of the water makes it more difficult for the latter to separate in the form of ice, just as it makes it more difficult for them to take the form of steam. It is impossible to dissolve a molecular weight (342 grams) of sugar in 100 grams of cold water but 34.2 grams lower the freezing-point by 1°.9 and the drop is proportional to the concentration, so that 342 grams would lower it by 19°. Here, also, the kind of molecule is without influence. 150 grams of glucose would produce the same drop of 19°, and so would 46 grams of alcohol ($C_2H_6O = 46$), for here there is no vaporization.

4. *A molecular weight in grams of any non-electrolyte, dissolved in* 100 *grams of water produces a lowering of the freezing-point of* 19°.

336. Liquids other than Water.—Solutions in other liquids act in the same way. Thus, if the molecular weight of a substance can be dissolved in 100 grams of alcohol it will produce a rise in the boiling-point of 11°.5. Fractions of a molecular weight produce a proportionate rise in the boiling-point. For 100 grams of acetic acid, the *molecular rise of the boiling-point* is 25° and the *molecular lowering of the freezing-point* is 39°.

The most important use of these facts is in determining the molecular weights of the countless new substances which are constantly being prepared. Thus, suppose that 1 gram of a substance, whose molecular weight was unknown, was found to lower the freezing-point of 100 grams of acetic acid 0°.5. We know that *the molecular weight, whatever it may be, would give a lowering of* 39°. Since the lowerings are proportional to the quantities of substance dissolved, we have·

$$0°.5 : 39° : : 1 : \text{Molecular weight}$$

From which the molecular weight = 78.

337. Solutions of Electrolytes.—Let us now experiment on the boiling-point of *salt-solution.* The molecular weight corresponding to the formula NaCl is 58.5. We dissolve one-tenth of this (5.85 grams) in 100 grams of water, expecting a rise in the boiling-point of about half of a degree. As a matter of fact, the solution boils at about 101°. The rise is nearly double what we should expect. A second portion of 5.85 grams sends the boiling-point up to nearly 102°. Molecule for molecule, salt has about twice as much effect on the boiling-point of water as has sugar.

Before we attempt to explain this puzzling fact, let us try some other electrolytes. Potassium chloride, so similar to salt in most respects, shows the same behavior. The molecular weight corresponding to KCl is 74.5 and 7.45 grams of it raise the boiling point of 100 grams of water about twice as much as the corresponding weight of sugar. Sodium hydroxide (NaOH = 40) and potassium hydroxide (KOH = 56) act in the same way. All four substances also lower the freezing-point of water nearly twice as much as does the equivalent quantity of sugar.

338. Ions.—When the sugar was split by inversion into glucose and fruit sugar the double number of molecules produced a double rise in the boiling-point. This suggests an explanation for the conduct of the salt solution. It seems that the rise in the boiling-point depends only upon the number of molecules of dissolved substance, and serves as a measure of this number. A double rise means that the number is doubled. But the salt molecule contains only two atoms, and the only way in which the number of molecules can be doubled is by the separation of each molecule into an atom of sodium and an atom of chlorine. *Thus the study of salt solution leads us straight to the conclusion that, when salt is dissolved in water, its molecules break up into atoms of sodium and atoms of chlorine, which move about in the liquid independently of each other.*

When the molecule of salt is broken up, the sodium atom takes up a positive charge of electricity, while the chlorine atom is negatively charged. These charged particles which are assumed to be present in solutions of electrolytes are called **ions,** a word due to *Faraday*, who laid the foundations of our knowledge of this subject. Their charges make them act very differently from ordinary atoms, as we shall see. The splitting of the molecule into charged fragments, which occurs when electrolytes are dissolved in water, is called **ionization.**

How does the electric current pass through a salt solution? The anode is simply a plate on which the dynamo or battery keeps a permanent positive charge. Unlike charges attract, so the negatively charged chlorine ions are drawn to the anode, where their charges are neutralized by its positive electricity. They then unite in pairs to form molecules of ordinary chlorine gas, which bubbles up from the anode.

In the same way, the negative charge on the cathode draws the positive sodium ions to it. When their charges are neutralized they are no longer ions. They are simply sodium atoms, which at once interact with the water, producing hydrogen, which escapes around the cathode, and sodium hydroxide, which dissolves.

The electrolysis of potassium chloride—which is carried out on a large scale in Germany with the sylvite from Stassfurt—is explained in the same way. We have only to substitute potassium ions for the sodium ions.

With the chloride of a metal like copper, which does not interact with water, matters are still simpler. The chlorine escapes at the anode, as before. At the cathode, the positive copper ions give up their charges and separate as ordinary copper, which forms a red plating on the cathode. Since the ions of all metals are, like those of sodium, positively charged, they always travel to the cathode. Hence, in electro plating, the object to be plated is always connected with the cathode.

339. Questions often Asked, with their Answers.—1. *Question:* Why can the current not get through a sugar-solution? *Answer:* In solutions, the current is carried only by the charged bodies we have called ions. As the boiling-point showed, the sugar dissolves as unbroken molecules. Therefore there are no ions to carry the current.

2. *Question:* If a salt solution contains free atoms of chlorine, why does it not smell of chlorine and bleach dye stuffs? *Answer:* The single charged atom which we call an ion of chlorine is a very different thing from the pairs of uncharged atoms in ordinary chlorine. There is no reason to expect it to act in the same way.

3. *Question:* Why do not the free sodium atoms in salt solution interact with the water, forming caustic soda and hydrogen? *Answer*: As in (2); the strong electric charge makes the sodium ion quite different from ordinary sodium. When the charge is given up at the cathode, the interaction *does* take place.

4. *Question:* How is it that salt is obtained unchanged when salt solution is evaporated? *Answer*: Ionization is reversible. Using $\overset{+}{\mathrm{Na}}$, where + means a positive charge, as a symbol for the sodium ion, and $\overline{\mathrm{Cl}}$ for the chlorine ion, we may write:

$$\mathrm{NaCl} \rightleftarrows \overset{+}{\mathrm{Na}} + \overline{\mathrm{Cl}}.$$

This equation is to be read forward when the salt is dissolved, and backward when it is separated by evaporation.

5. *Question*: Are all the salt molecules separated into ions, or are there some unbroken molecules (NaCl) mixed with the ions in the solution? *Answer:* In a concentrated salt solution there are many unchanged molecules mixed with the ions. The more the solution is diluted the more complete the ionization becomes. When a molecular weight (58.5 grams) of salt is dissolved in a liter of water, something like one-third of the total number of

molecules remains un-ionized. If the solution is diluted to 20 liters, the separation into ions becomes almost complete.

6. *Question:* Is it possible to separate the two kinds of ions, and to obtain, for instance, a liquid containing only sodium ions in one vessel and a liquid containing only chlorine ions in another? *Answer:* No, the attraction of the positive and negative charges prevents any separation of this sort. Thus, suppose that in some way, we *had* succeeded in separating the sodium and chlorine ions from only 58.5 milligrams (0.0585 gram) of salt. A simple calculation shows that, even if the two vessels containing the ions were a kilometer apart, the attractive force between them would be equal to the weight of 8,500,000 kilograms. The separation of such quantities of electricity would produce disturbances which would make the most violent thunder storm a tame affair by comparison.

340. Ions of Bases and Acids.—A solution of sodium hydroxide is a good conductor, and the freezing- and boiling-points are altered about twice as much as they would be by the equivalent quantities of sugar. Therefore each molecule has split into two ions. Just as in salt solution, the positive charge is taken by the sodium atom. Then the negative charge must be taken by the rest of the molecule, which is the *radical* OH. The ions in sodium hydroxide solution are therefore $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{OH}}$. In potassium hydroxide solution they are $\overset{+}{\mathrm{K}}$ and $\overset{-}{\mathrm{OH}}$. The peculiar and very similar properties of the two solutions are due to the $\overset{-}{\mathrm{OH}}$, which is called **hydroxyl.**

Hydroxyl is the characteristic ion of bases. It is present in the solutions of all of them, and since it is the only constituent which is common to them all, the bitter taste, the caustic action on organic matter, the corrosive action on certain metals, the effect on litmus and other dye stuffs and the interaction with acids must be ascribed to its presence.

In a water solution of hydrochloric acid, the ions can only be $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{Cl}}$. The hydrogen ion, $\overset{+}{\mathrm{H}}$, is quite a different thing from hydrogen gas, H_2. Thus, it is not combustible. It can only be obtained in water solution, while H_2, as we know, is scarcely soluble in water. Hydrogen is tasteless, but $\overset{+}{\mathrm{H}}$ has an intensely sour taste.

The ions of nitric acid are $\overset{+}{H}$ and $\overline{NO_3}$. **The hydrogen ion is the characteristic ion of acids**; it is the only constituent which is common to water solutions of all of them and therefore the properties which they all have in common, the sour taste, the corrosive action on most metals, the effect on litmus and other dyes and the interaction with bases must be ascribed to its presence.

341. Comparison of the Hypothesis with the Facts.—Three ways of testing this far-reaching conclusion suggest themselves:

1. A solution of hydrogen chloride in the hydrocarbon *toluene* C_7H_8 does not affect the color of litmus and has no action on the metals. Then it ought not to contain any hydrogen ions. But if so, it cannot contain chlorine ions either; it must be a non-conductor. Experiment shows that it does, in fact, obstruct the passage of the current just as completely as a water solution of sugar. Pure liquid hydrogen chloride, free from water, acts in the same way: it is inactive toward litmus and the metals and is a non-conductor.

2. Different acids act upon metals, like zinc, with very different speeds. For fair comparison the solutions of different acids should be made to correspond in concentration. *Active* acids like hydrochloric, liberate hydrogen *rapidly* in contact with zinc. *Inactive* acids, like acetic, liberate hydrogen *much more slowly*, under similar conditions. If we are right in ascribing the chemical activity of acids to the hydrogen ions this can have only one meaning. There must be *more hydrogen ions* in the solution of hydrochloric acid. A larger proportion of its molecules must be separated into ions than in the acetic acid.

Then the solution of hydrochloric acid ought to be a better conductor than that of acetic acid at equivalent concentration. We have already seen that this prediction is verified. *Active* acids, like hydrochloric, conduct *well*, *inactive* ones, like acetic, *badly*, when dissolved in water.

3. The *thermochemical* equations for the neutralization of hydrochloric and nitric acids in dilute solution, by caustic soda and caustic potash are as follows:

$$
\begin{array}{llllll}
(1) & NaOH + HCl & \longrightarrow & NaCl + H_2O + 13{,}700 \text{ Cal.} \\
(2) & KOH + HCl & \longrightarrow & KCl + H_2O + 13{,}700 \text{ Cal.} \\
(3) & NaOH + HNO_3 & \longrightarrow & NaNO_3 + H_2O + 13{,}700 \text{ Cal.} \\
(4) & KOH + HNO_3 & \longrightarrow & KNO_3 + H_2O + 13{,}700 \text{ Cal.}
\end{array}
$$

The fact that *identical amounts of heat* are produced in all four cases is surprising. Even in changes so similar as the syntheses of salt and of sylvite the heat values are different:

$$\begin{array}{llll} (5) & \mathrm{Na} + \mathrm{Cl} \longrightarrow & \mathrm{NaCl} + & 98{,}000 \text{ Cal.} \\ (6) & \mathrm{K} + \mathrm{Cl} \longrightarrow & \mathrm{KCl} + & 106{,}000 \text{ Cal.} \end{array}$$

We must find some explanation for the fact that, while the heat values of (5) and (6) are different, those of (1) and (2) are identical. This would indicate that (1) and (2) are, in reality, more nearly alike than a mere glance at the equations would lead us to think.

Let us now apply the idea of ions to (1)

The NaOH becomes $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{OH}}$.
The HCl becomes $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{Cl}}$.
The NaCl becomes $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{Cl}}$.
The H_2O remains H_2O (being practically un-ionized)

The equation becomes:

$$\overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}} \longrightarrow \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}} + \mathrm{H_2O}.$$

But the $\overset{+}{\mathrm{Na}}$ *and the* $\overset{-}{\mathrm{Cl}}$ *have taken no part in the chemical change.* They are simply left over and can be subtracted from both sides of the equation, which then becomes:

$$\overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}} \longrightarrow \mathrm{H_2O}.$$

Hydroxyl ions and hydrogen ions have combined to form water, and that is all that has happened. If we evaporate the solution the $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{Cl}}$ will form NaCl, but that does not occur in dilute solution.

Similar treatment of (2) gives:

$$\overset{+}{\mathrm{K}} + \overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}} \longrightarrow \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{Cl}} + \mathrm{H_2O}.$$
$$\overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}} \longrightarrow \mathrm{H_2O}.$$

We can now state the reason for the identical heat values: *the two changes are, at bottom, the same.*

(3) and (4) can be handled in the same way:

$$\text{(3)}\ \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{NO_3}} \longrightarrow \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{NO_3}} + \mathrm{H_2O}.$$

$$\overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}} \longrightarrow \mathrm{H_2O}.$$

$$\text{(4)}\ \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{NO_3}} \longrightarrow \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{NO_3}} + \mathrm{H_3O}$$

$$\overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}} \longrightarrow \mathrm{H_2O}.$$

342. General Statement.—Remembering that *active,* in this connection, means *completely ionized,* we may put the whole matter thus:

When an active base is neutralized, in dilute solution, by an active acid the only change is the union of hydroxyl ions and hydrogen ions to water. The heat value is, therefore, always the same:

$$\text{(7)}\ \overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}} \longrightarrow \mathrm{H_2O} + 13{,}700 \text{ Cal.}$$

(7) Can be regarded as a general equation, which applies to all cases of neutralization, where the base and the acid are almost completely ionized.

343. Normal Solutions.—From (7) it is plain that, in round numbers, 1 gram of hydrogen ion interacts with 17 grams of hydroxyl ion. A water solution of an acid which is of such strength that it contains 1 gram of hydrogen ion per liter is called a *normal solution.* Such a solution would contain 36.5 grams of pure hydrochloric acid per liter, or 63 grams of pure nitric acid. The choice of the acid is a matter of convenience. *Oxalic* acid may be used in the laboratory studies. In that case the normal solution is made by simply weighing out 63 grams of oxalic acid, the quantity which will yield 1 gram of hydrogen ion. This is then dissolved, and diluted to a liter in a flask with a graduation on the neck.

From (7) it appears that a liter of this liquid will neutralize that quantity of any base which contains 17 grams of hydroxyl ion, that is, 40 grams of sodium hydroxide, NaOH, or 56 grams of potassium hydroxide, KOH. One cubic centimeter of it will neutralize $\frac{1}{1000}$ of these quantities, that is, 40 milligrams (0.040 grams) of sodium hydroxide, or 56 milligrams (0.056 gram) of potassium hydroxide.

Normal solutions are constantly used by the working chemist. Thus, suppose it is required to ascertain how much real sodium hydroxide there is in a commercial sample of impure caustic soda. One gram of the caustic soda is weighed and dissolved. A few drops of litmus are added, which will turn the liquid blue. Then the normal acid is added from a burette (Fig. 80) with constant stirring. When all the sodium hydroxide is neutralized, the liquid will turn red. Then the number of cubic centimeters of normal acid used are read off. Suppose, for illustration, that 22.5 c.c. of the normal acid were required. Then 0.040 × 22.5, or 0.900 gram of sodium hydroxide must have been neutralized. The caustic soda, therefore, contained only 90 per cent. of real sodium hydroxide, the remaining 10 per cent. being water and other substances.

A *normal solution of a base* contains 17 grams of hydroxyl ion per liter. Such a solution would contain 40 grams of sodium hydroxide in a liter. One cubic centimeter of it neutralizes 0.0365 gram of hydrochloric acid, 0.063 gram of nitric acid or equivalent quantities of other acids.

The word **alkali** means a solution containing a base. The sensitive dye stuffs, used in such experiments are called **indicators.** Litmus is an example. There are many others. Cochineal is orange with acids and violet in solutions containing bases. Phenol-phthalein is colorless in acid solution and red when the liquid contains a base.

Definitions

Electrolysis. Decomposition of a compound by the electric current.

Base. A substance which tastes bitter, turns red litmus *blue* and interacts with acids forming, with each acid, water and a salt. A base is a *hydroxide*, usually of a *metal*, sometimes of a radical.

Electrolyte. A substance whose solution in water conducts the electric current. Only acids, bases and salts are electrolytes.

Ions. Fragments bearing electric charges, into which the molecules of electrolytes are separated in water solutions.

Ionization. The separation of the molecules into ions, which takes place when acids, bases or salts are dissolved in water.

Indicator. A sensitive dye-stuff, like litmus, whose color is strikingly changed by traces of acids or bases.

Alkali. A solution which contains a base, and which, therefore, reverses the color-changes in indicators produced by acids.

CHAPTER XXI

ELEMENTS WHICH RESEMBLE CHLORINE: IODINE, BROMINE, FLUORINE

344. **Halogens.**—The four elements chlorine, iodine, bromine and fluorine are called the *halogen* group. *Tincture of iodine,* a deep brown liquid used as an application for sprains, is familiar to the student. Like all of the druggist's tinctures, it is a solution in alcohol. The dissolved substance is the element *iodine,* which was discovered by *Courtois,* a Parisian saltpeter maker, in 1811.

345. **Properties of Iodine.**—Some facts concerning iodine are summarized in the following table:

Appearance: flat, black-gray crystals with about the color and luster of graphite.
Boiling-point: 184°.
Molecular weight: 22.4 liters of the vapor calculated to S.T.P. weigh 254 grams.

Symbol: I.
Atomic weight: 127.
Melting-point: 114°.
Color of vapor: deep purple.
Formula: I_2.

Solubility: 100 c.c. water dissolves only 0.016 gram of iodine. It is freely soluble in a water solution of potassium iodide (forming a brown solution), in alcohol (tincture of iodine), in ether (brown solution), in chloroform (purple) and in carbon disulphide (purple).
Chemical conduct: active, but less so than the other three members of the group.
Valence: iodine, like the other halogens is *univalent* toward hydrogen and the metals. Toward non-metals the valence is variable.
Uses: for making potassium iodide which is largely employed in medicine, and iodoform (CHI_3) which is a yellow powder used to dress wounds in surgery; in the manufacture of complex carbon compounds which are employed as dye stuffs.
World's annual production: about 500 tons, mostly from Chili, where iodine compounds occur as an impurity in the great deposits of sodium nitrate (Chap. XXIII)..

346. **Hydriodic Acid.**—*Hydrogen iodide,* HI, resembles hydrogen chloride. It is a colorless, suffocating gas, very

soluble in water and the solution is a good conductor and an active acid. Hence the molecules must be largely separated into $\overset{+}{H}$ and $\overset{-}{I}$.

That iodine is less active than chlorine is plain when the behavior of a mixture of equal volumes of hydrogen and iodine vapor is studied. The union is sluggish and partial. At 450°, four-fifths of the two elements unite to hydrogen iodide; the rest remains in the free state no matter how long the mixture is heated. That this is merely another case of equilibrium dependent upon concentration, is proved when hydrogen iodide alone is heated to 450°. The purple vapor of iodine appears and one-fifth of the gas separates, producing a mixture of exactly the same composition as that obtained by heating iodine vapor and hydrogen to the same temperature.

Hydrogen iodide burns in oxygen, forming purple fumes of iodine. Water is also formed:

$$2\,HI + O \longrightarrow H_2O + I_2.$$

The solution is slowly acted upon in the same way by the oxygen of the air and turns brown from the iodine liberated.

Related to this behavior is the fact that hydrogen iodide cannot be made by the action of sulphuric acid upon an iodide, like potassium iodide. The oxygen of the sulphuric acid oxidizes the hydrogen iodide, so that iodine is the chief product, very little hydrogen iodide being obtained. The water solution of hydrogen iodide is called *hydriodic acid.* It can be made by passing hydrogen sulphide into water in which powdered iodine is suspended:

$$H_2S + I_2 \longrightarrow 2\,HI + S.$$

The sulphur is removed by filtration. Hydriodic acid is employed in medicine.

347. **Potassium Iodide.**—*Potassium iodide,* KI, which is largely used in medicine, is the most important iodine compound. It forms colorless cubes, which slowly turn yellow in the air from separated iodine. Its specific gravity is 3. It melts at 700°, and 100 c. c. water dissolves, at 18°, 138 grams of it. It is also soluble in alcohol.

348. Tests for Iodine.—When chlorine is passed into a solution of potassium iodide, the colorless liquid turns brown and a gray-black powder of iodine separates. Solutions of other iodides act in the same way, for the metal ions play no part. The chlorine takes the negative charges from the iodine ions, converting them into ordinary iodine:

$$2\overline{\mathrm{I}} + \mathrm{Cl}_2 \longrightarrow 2\,\overline{\mathrm{Cl}} + \mathrm{I}_2.$$

Iodine can be obtained from *seaweed* by treating a water solution of the ashes with chlorine.

Sometimes traces of iodine, insufficient to color the water must be tested for. In such cases, after passing in a little chlorine, chloroform is added and the mixture shaken. The chloroform dissolves the iodine and forms a purple layer at the bottom of the mixture. This makes the test more delicate, because almost all the iodine can be collected in a few drops of chloroform.

Or, the starch test, which is wonderfully delicate, can be used. Iodine ions (solutions of iodides) do not affect starch, but iodine molecules (free iodine) dye starch intensely blue. A little starch paste made by boiling starch with water, is mixed with the solution suspected of containing iodine ions. If the latter are really present, a little chlorine will now produce a deep blue color which serves to identify the merest traces of iodine. We have seen (p. 191) that iodine solution can be used as a test for starch.

349. Bromine: Discovery.—In the extraction of salt from sea water (p. 206), the liquid is evaporated to about one-twentieth of its original volume. The liquid which remains when the salt has separated is called the *mother liquor* of the salt crystals. Those substances which are present only in traces in sea water remain dissolved, when the salt separates, and the mother liquor contains them, in twenty-fold the original concentration.

In 1826 *J. A. Balard* made some experiments with the mother liquor of the salt basins at Montpellier, in southern France near the Mediterranean. He found that chlorine gas produced a red color in the liquid. He then distilled and obtained a dense red liquid which proved to be a new element. It had such an offensive odor that it was named *bromine* from the Greek word for *stench.* Sea water contains bromine ions, and in Balard's experiments, the chemical change was similar to the action of chlorine upon a solution of an iodide. The chlorine took the negative charge from the bromine ions:

$$2\,\overline{\text{Br}} + \text{Cl}_2 \longrightarrow 2\,\overline{\text{Cl}} + \text{Br}_2.$$

350. **Preparation.**—The mother liquor of the Stassfurt salt deposits contains bromine ions. So does the mother liquor from salt wells in Ohio, Michigan and Kentucky. These two sources divide the world's production about equally.

In one method of extraction, the liquid is allowed to drip through a sandstone tower packed with cylinders of fire brick. Chlorine gas, obtained from a cylinder of liquid chlorine, is passed in at the bottom. The liquid containing the dissolved bromine flows into a vessel made of granite slabs, where it is heated by steam, to separate the bromine by distillation. The bromine is condensed in another vessel.

351. **Properties of Bromine.**—The following table gives some information about bromine:

Symbol: Br.
Formula: Br_2.
Atomic weight: 80.
Specific Gravity: 3.
Melting-point: –7°.
Boiling-point: 63°.
Appearance: Dark red liquid.
Solubility: 100 c.c. water at 18° dissolves 3 grams; it is more soluble in ether, carbon disulphide and chloroform, which therefore extract it from water as they do iodine, but less completely. All these solutions are red.

Bromine has a severe caustic action on the skin, which it stains yellow. It gives a yellow color with starch paste, but the test is not delicate. Its vapor is red and escapes freely from the liquid even in the cold. The vapor has an unbearable smell, and sharply irritates the eyes, nose and throat.

Bromine is an *active* element, more so than iodine, but it is less active than chlorine. It forms bromides upon contact with the metals. In many cases the combination is violent. Tin burns brightly when dropped into bromine, and potassium explodes. In most respects bromine stands between chlorine and iodine, but the fact that no *oxide* of bromine exists is a point in which it resembles fluorine (see below).

Bromine finds its chief uses in the manufacture of potassium bromide and of complex carbon compounds which are to serve as dye-stuffs, drugs or perfumes. It is a good bleaching agent and an excellent disinfectant, but is never employed for these purposes. (Why not?)

352. **Hydrobromic Acid.**—*Hydrogen bromide*, HBr, closely resembles hydrogen chloride. It is a colorless, suffocating gas. 100 c.c. water dissolves 60 liters of it at 10°. The solution is an active acid.

353. **Potassium Bromide and Sodium Bromide.**—*Potassium bromide*, KBr, is the most important bromine compound. It forms white cubes, freely soluble in water. It is much employed in photography.

Sodium bromide, NaBr, resembles potassium bromide. Both are extensively used in medicine, for disorders of the nervous system.

354. **Fluorine: Fluor spar.**—The common mineral *fluor spar* is found in transparent cubes, which are often violet, yellow or green. It frequently occurs with ores of the metals, especially of lead. The crystals are soft enough to be scratched with a knife point, and this serves to distinguish fluor spar from other minerals which resemble it, but are harder.

355. **Chemical Nature of Fluor spar.**—When a bit of fluor spar is held in the Bunsen flame, it melts easily (hence the name from the Latin *fluere*, to flow) and colors the flame bright orange. The color will be familiar to the student, for the light of the *flaming arc lamps*, which have become so common, has the same shade. The "carbons" of these lamps are made of a mixture of carbon with fluor spar and other substances.

This orange flame-color is a test for the element **calcium,** a grayish white metal, which resembles sodium, but is harder and less active. We shall study it in Chap. XXIV.

Calcium, then, is the metallic constituent of fluor spar. The non-metallic constituent cannot be obtained by direct decomposition of the mineral, for the elements of fluor spar are so firmly united that *direct* separation is impossible.

356. Hydrofluoric Acid.—The behavior of fluor spar with *sulphuric* acid indicates clearly that it is similar in chemical nature to table-salt, that is, that the calcium is combined with an element which resembles chlorine. A little of the powdered mineral can be heated gently with strong sulphuric acid in a lead dish. The colorless, poisonous gas which escapes smells like hydrogen chloride, produces a white cloud with a glass rod wet with ammonia, and reddens blue litmus paper. It is *hydrogen fluoride*, HF, the hydrogen compound of *fluorine*, which is the non-metallic element of fluor spar.

If the dish containing the fluor spar and sulphuric acid is covered with a glass plate, the lower surface becomes white and opaque. Glass is rapidly attacked by hydrogen fluoride, and use has been made of this fact for more than two centuries, in the **etching** of glass. Either hydrogen fluoride, or its solution in water can be used for this purpose. The glass is covered with wax, which is not attacked by the acid, and the pattern is cut through the wax with a sharp instrument which lays bare the glass. Exposure to hydrogen fluoride will then etch the pattern permanently upon the object.

To obtain a water solution of hydrogen fluoride, the mixture of fluor spar and sulphuric acid can be heated in a lead retort, and the gas passed into water contained in a lead vessel.

The solution is a colorless, acid liquid, similar to hydrochloric acid. It is called *hydrofluoric acid.* It dissolves many metals, forming fluorides, with escape of hydrogen:

$$Zn + 2\,HF \longrightarrow ZnF_2 + H_2.$$

These interactions are not as rapid as those of hydrochloric acid under the same conditions, for hydrofluoric is a much less active acid and the solution contains little $\overset{+}{H}$ and $\overset{-}{F}$ and much un-ionized HF. For this reason, the solution is a poor conductor.

Great care must be taken not to get hydrofluoric acid on the skin, upon which it produces dangerous wounds. It is kept in bottles of hard paraffine, on which it has no action.

357. Fluorine.—It is a difficult and dangerous matter to make hydrogen fluoride *free from water.* Anhydrous hydrogen fluoride is a colorless liquid, which must be kept in a freezing mixture, for it boils at 19°. It is a non-conductor, but when it contains dissolved potassium hydrogen fluoride (KHF_2) the $\overset{+}{K}$ and $\overset{-}{F}$ ions carry the electric current through the liquid. At the cathode, the potassium interacts with the hydrogen fluoride, liberating hydrogen; at the anode, *fluorine,* the non-metallic element of fluor spar, escapes.

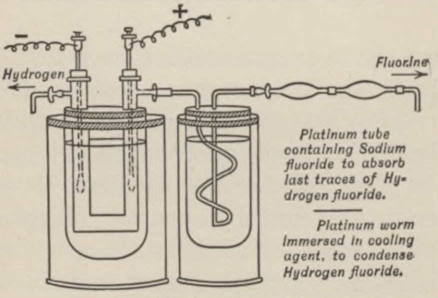

Fig. 82.—The isolation of fluorine.

Fig. 82 is a diagram of the apparatus used by *Moissan,* who isolated fluorine in 1886, overcoming the difficulties which had baffled chemists for a century. The U-shaped tube contained 100 c.c. of the solution of potassium hydrogen fluoride in anhydrous hydrogen fluoride. For his first experiments, the apparatus was made of platinum; later he found that copper, which is only slightly attacked by fluorine, could be used. The electrodes are of platinum and the stoppers, through which they pass, of fluor spar, which is unaffected by fluorine. (Why?) The U-tube is immersed in liquid methyl chloride, which is made to evaporate rapidly by a current of air. This keeps the temperature down to −50°; otherwise the hydrogen fluoride would boil away, owing to the heat produced by the passage of the electric current.

The hydrogen is simply allowed to escape from the side tube in the cathode limb. None of it must be allowed to get over into the anode limb, for violent explosions would result. The fluorine is led through a platinum coil cooled to –50° to condense any hydrogen fluoride which it contains, and then through platinum bulbs containing sodium fluoride, NaF, which absorbs the last traces of hydrogen fluoride. It then passes into the platinum or fluor spar tube containing the substance whose interaction with it is to be studied. In many cases, glass test tubes can be used, for pure fluorine has little or no action on glass.

358. Properties of Fluorine.

—Some information concerning fluorine is summarized in the following table:

Symbol: F.	**Boiling-point:** −187°.
Formula: F_2.	**Freezing-point:** −223°.

Atomic weight: 19.
Color: Similar to that of chlorine, but paler.
Odor: Similar to that of chlorine.
Action on the Body: Irritates eyes and respiratory passages.
Chemical conduct: Most active of the elements. Combines directly with most other elements, and the combination is attended, in many cases, with combustion.
Liquid fluorine is yellow and has about the same specific gravity as water.

Fluorine acts violently upon most *compounds*. When it is passed into a test tube containing a little table salt, chlorine gas and sodium fluoride are produced:

$$NaCl + F \longrightarrow NaF + Cl.$$

Other chlorides behave in the same way. In the case of bromides, the bromine which is liberated at first, burns in the fluorine to a fluoride of bromine. Iodides behave like bromides.

As a rule, chemical changes become so slow at very low temperatures that practically they may be said not to occur at all. Substances which interact vigorously at room temperature may be left in contact at –200° without any apparent effect. It is noteworthy, therefore, that liquid fluorine still takes part in violent chemical changes when cooled by boiling liquid air (–190°). This is a striking instance of the chemical activity of fluorine. When liquid fluorine is spilled on a wooden floor, a flame appears which is due to the combination of the fluorine with the hydrogen of the wood.

359. Occurrence.

—Like the other members of the chlorine group, fluorine scarcely occurs in the free state. Its compounds are much more abundant than those of bromine or iodine. *Traces* of fluorine compounds are contained in river and sea-water, in the bones (especially the enamel of the teeth) and in many plants.

The chief mineral containing fluorine is fluor spar (see above) which is *calcium fluoride*, CaF_2. Fluor spar serves as the raw material for the manufacture of hydrofluoric acid, and is also used in the making of opal glass. Fluor spar is added to the melted glass. On cooling it separates in countless little crystals which render the glass cloudy.

Another important compound is *cryolite*, Na_3AlF_6, which is a white mineral with a greasy luster, found in Greenland. It has been referred to in connection with the manufacture of aluminium (p. 129). It is used in making alum (Chap. XXII). Cryolite is much used, in the same way as fluor spar, in the preparation of opal glass.

Related Topics

360. The Halogens as a Group of Elements.—We have seen that the members of the chlorine group unite with the metals, producing compounds more or less like table-salt. Hence they are called the *halogens*, which is from the Greek, and means *salt-formers*.

The fact that the activity of the halogens increases with decreasing atomic weight from iodine ($I = 127$) to fluorine ($F = 19$) has been pointed out. This is especially clear (1) from their combination with hydrogen to form the acids of the formula HI, HCl, HBr and HF, and (2) from the interaction of some of the halogens with water, forming the same acids, with escape of oxygen, for instance:

$$H_2O + Cl_2 \longrightarrow 2\,HCl + O.$$

The heat values in (3), in the following table, refer to the simple equations like

$$H + Cl \longrightarrow HCl$$

in which single atomic weights unite. The iodine and bromine are supposed to be used in the form of *vapor*. The increase in the chemical energy with decreasing atomic weight is strikingly shown in the heat value, which is about 100 times as great for fluorine as for iodine, although the actual weight of fluorine used is only about one-seventh of that of the iodine.

(1) *Element*	(2) *Behavior with Hydrogen*	(3) *Heat Value of* (2)	(4) *Behavior with Water*
Iodine	Slow, partial combination when heated.	400 Cal.	No interaction.
Bromine	Complete combination when heated. No explosion with flame or in sunlight.	12000 Cal.	Slow escape of oxygen in sunlight.
Chlorine	No action in dark. Explodes in sunlight or when flame is applied.	26000 Cal.	Oxygen escapes in sunlight more rapidly than in the case of bromine.
Fluorine	Explodes at once even in the dark and without flame being applied.	39000 Cal.	Explosive liberation of oxygen [as ozone (1)] even in the dark.

361. Photography.—Silver chloride darkens when exposed to light. Chlorine escapes and the dark substance formed is at first silver *sub-chloride* Ag_2Cl:

$$2\,AgCl \longrightarrow Ag_2Cl + Cl.$$

Later, if the exposure to light continues, the sub-chloride loses its chlorine, leaving silver:

$$Ag_2Cl \longrightarrow 2\,Ag + Cl.$$

Talbot, in 1839, showed how this fact could be used for picture-making. If a paper is dipped in a solution of table salt and then in one of silver nitrate $Ag\,NO_3$, silver chloride is formed in the paper·

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3, \text{ or } \overset{+}{Ag} + \overset{-}{Cl} \longrightarrow AgCl.$$

The paper must then be kept in the dark, for it is sensitive to light. If a semi-transparent object, like the wing of a butter-

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[1] Ozone is a form of oxygen which will be studied in Chap. XXIV.

fly, is pressed out against a glass plate, with a piece of sensitive paper back of it, and exposed to light, a copy will be obtained, but it will be dark where the wing is light and light where the wing is dark. Where there is a dark spot, little light will get through the wing, and a white area on the paper will result, but a clear area allows much light to pass and strongly blackens the paper beneath.

Another difficulty in making pictures in this way is that they can only be examined by candlelight. On account of the unchanged silver chloride in them, the white portions are still sensitive to light, and, if exposed, the whole picture soon turns black. Photographers' "proofs" act in the same way, for the same reason.

Talbot overcame this difficulty by soaking the picture in a strong solution of table-salt. This dissolves the silver chloride out of the paper, and, of course, the sensitiveness to light goes with it. The astronomer Herschel afterward found that a solution of "*hypo*" was better than salt solution. "Hypo" is sodium thiosulphate, $Na_2S_2O_3$. Its solution rapidly dissolves silver chloride and silver bromide.

362. Silver Bromide.—*Silver bromide* is a yellow-white substance, "insoluble" in water (100 c.c. water dissolves 0.00001 gram). It forms when silver ions and bromide ions come together, for instance:

$$AgNO_3 + KBr \longrightarrow AgBr + KNO_3.$$

or, since any soluble silver salt and any soluble bromide will answer:

$$\overset{+}{Ag} + \overset{-}{Br} \longrightarrow AgBr.$$

Exposure to light for even a small fraction of a second has a remarkable effect upon silver bromide. The appearance of the salt is unchanged, but *it is much more easily converted into silver than before.* Modern photography is based upon this fact.

There are complex carbon compounds, like *pyrogallol,* which are called, by the photographer, *developers.* Upon silver bromide which was made in the dark, and has never been exposed to light, pyrogallol solution has only a very slow action; but silver bromide, which has been acted upon by light for even a hundredth of a second, is rapidly converted into metal by it.

A photographic plate is a glass rectangle, one surface of which is covered with a film of hardened gelatin containing silver bromide. In the manufacture, the gelatin is dissolved in warm water and ammonium bromide and silver nitrate added:

$$AgNO_3 + NH_4Br \longrightarrow AgBr + \underset{\substack{\text{Ammonium}\\\text{nitrate}}}{NH_4NO_3}.$$

The liquid is kept warm for a time, during which the fine amorphous silver bromide which is first formed collects into larger crystalline grains. This is called "ripening" and greatly increases the sensitiveness of the plates. Then the mass is allowed to cool to a jelly which is cut up, and the ammonium nitrate removed by washing with water.

After drying and remelting, the "emulsion," as it is called, is poured upon glass plates, which, when dry, are ready to be packed in light-proof boxes. The whole manufacture is conducted in a dim red light, too weak to affect the emulsion. *Films* are made in the same way, except that the backing is transparent celluloid, instead of glass.

In taking a picture, the plate is placed in the camera, in such a way that the sensitive surface is in the focus of the lens. After the exposure to light, the plate looks just the same as before. But when it is *developed,* a black deposit of *silver* is produced wherever the light has acted.

The next step is to dissolve and remove the unaltered silver bromide, to prevent it from being acted on by light, which would turn the whole plate black. This is called "fixing" and is accomplished by soaking the plate in a solution of sodium thiosulphate ("hypo").

The thoroughly washed and dried plate is now called a *negative.* One reason for this name is that the lights and shadows of the original are reversed in it. The light portions in the original are represented by blackish silver, while the dark areas in the original are clear glass in the negative. Another reason for the name is that the arrangement from right to left is reversed in the negative, which, in this respect, is like a mirror-image.

In *printing,* the negative is exposed to light with a piece of sensitive paper back of it, in contact with the image. The light passes easily through the clear portions, which therefore become dark in the print, but is arrested by those parts which are covered with opaque silver, which remain white on the paper. Hence the lights and shadows are again reversed and, with care, can be made the same in the print as in the original.

Various papers are employed for printing. A very common kind is covered with a film of starch or egg-albumin containing silver chloride. When such paper is exposed to sun-light, silver is rapidly produced, so that the progress of the printing can be followed by inspection, but the picture has an unpleasant reddish color. If the print is afterward dipped into a solution containing gold chloride, part of the silver of the image is replaced by gold, which darkens it to a more satisfactory tint. This process is called *toning*.

The "developing" papers, like "Velox," work on the same principle as a plate. The sensitive layer is a film of gelatin containing silver bromide or chloride, and, when briefly exposed back of a negative, the paper remains white, but the picture appears upon dipping it into the developer. The light of a Welsbach mantle or an incandescent lamp can be used. The print needs no toning.

Both these kinds of paper require "fixing" after the picture appears. The unaltered silver chloride or silver bromide, as the case may be, must be removed, otherwise the whole print would shortly turn black. This is accomplished in the same way as with a plate, by soaking in a solution of sodium thiosulphate, and washing.

In platinotypes, the picture consists of finely divided platinum, and in some carbon prints, of lampblack. Both have the merit of absolute permanence, since both platinum and carbon are unaffected by the air.

Definitions

Flaming arc lamp. A lamp in which most of the light is radiated, not from the carbons, but from a mass of incandescent vapor between them.

Halogen. One of the four members of the chlorine group of elements.

Developer. A substance whose behavior toward silver bromide depends upon whether the silver bromide has been exposed to light or not. If the silver bromide has been exposed to light, a developer rapidly converts it into silver; if not, the developer does not affect it.

Emulsion. A solution of gelatin containing suspended silver bromide, ready for use in the manufacture of photographic plates or films.

Fixing. Soaking an exposed and developed plate in a solution of "hypo" to remove the unchanged silver bromide.

Negative. The product obtained by exposing, developing and fixing a photographic plate.

Toning. Altering the color of a photographic print by a chemical process.

BOOK V

ACIDS CONTAINING OXYGEN, AND THEIR SALTS

INTRODUCTION

Here we leave the compounds containing only *two* elements, which have, with some necessary exceptions, furnished the main subject matter of the first four books, in order to devote ourselves to the study of some important compounds containing *three* elements.

The most important of these compounds, which fall within the scope of an elementary treatment of our science, are the acids containing oxygen, and the salts of these acids. Sulphuric acid, nitric acid, carbonic acid, boric acid, phosphoric acid, silicic acid and their salts are the subjects to which we shall now give our attention. Many of these compounds have not only scientific, but also practical interest. Some of them form the foundation of great industries.

We shall then discuss, very briefly, some important compounds containing the *four* elements carbon, hydrogen, oxygen and nitrogen. The concluding chapters will be devoted to the classification of the elements and to the subject of chemical calculations.

CHAPTER XXII

SULPHURIC ACID AND ITS SALTS.—HYDROLYSIS.—THE ELECTROLYSIS OF DILUTE SULPHURIC ACID

363. Behavior of Sulphur Trioxide with Water.—When the silky white needles of sulphur trioxide SO_3 (p. 97) are dropped into water, explosive interaction occurs and much heat is evolved. When the liquid cools, it is found to redden blue litmus, to act upon metals liberating hydrogen, and to conduct the electric current. It contains, therefore, an *active acid* to which the name **sulphuric acid** has been given.

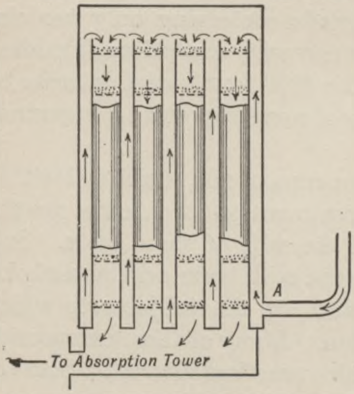


FIG. 83.—Preparation of sulphuric acid by the contact process

Direct combination of the sulphur trioxide and water must have occurred, for no gas escapes and the liquid contains nothing but a solution of sulphuric acid. The simplest interpretation of these facts is the equation:

$$SO_3 + H_2O \longrightarrow H_2SO_4.$$

Analysis of sulphuric acid and its salts, which are called the *sulphates,* shows that H_2SO_4 is, in fact, the correct formula of the acid, and that the sulphates are formed by the replacement of one or both atoms of hydrogen by metals.

364. "Contact Process" for Sulphuric Acid.—Sulphuric acid is largely made from sulphur trioxide and water, the sulphur trioxide being obtained by the method described on p. 96. The first step in the process is to burn pyrite, FeS_2, in furnaces, with more air than is necessary, so that the gases produced contain an excess of oxygen along with the sulphur dioxide. After being cooled and carefully purified, the gases enter at *A*, the bottom of the "contact apparatus" (Fig. 83), which is an upright cylinder containing four tubes, fitted with perforated shelves. Upon each shelf is a layer of asbestos, coated with platinum powder. The gases pass upward around the outside of the tubes, and enter them at the top. The object of this arrangement is to cool the tubes. This is necessary, because the chemical change which takes place in them evolves much heat:

$$SO_2 + O \longrightarrow SO_3 + 23{,}000 \text{ Cal.}$$

Another advantage is that the gases are warmed to the proper temperature (400°) before they enter the tubes.

Laden with fumes of sulphur trioxide, the gas passes into the bottom of the *absorption tower*, down which strong sulphuric acid trickles. This rapidly and perfectly absorbs the sulphur trioxide, which dissolves in the acid. By cautiously diluting this solution with water, sulphuric acid of any desired strength can be made.

365. Tests for Sulphuric Acid.—A solution of *barium chloride* $BaCl_2$ is added to some dilute sulphuric acid. A white *precipitate* of barium sulphate $BaSO_4$ is formed:

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\,HCl.$$

However, a solution of any sulphate will give the same precipitate when barium chloride is added. The test is for the $\overset{--}{SO_4}$ ion. Hence we may write:

$$\overset{--}{SO_4} + \overset{++}{Ba} \longrightarrow BaSO_4.$$

Sulphuric acid can be distinguished from a *sulphate* by adding a pinch of sugar and evaporating almost to dryness. Sulphates have no effect, but sulphuric acid blackens the sugar, producing impure charcoal.

366. The Lead Chamber Process for Sulphuric Acid.—Some water, which has been warmed until it gives off vapor freely, is poured into a liter flask. A little powdered sulphur is heated in an iron spoon until it begins to burn and is then held in the flask until the air in the latter is charged with sulphur dioxide, when it is withdrawn.

The mixture of gases in the flask now contains sulphur dioxide, SO_2, water, H_2O, and oxygen from the air. These substances might interact to form sulphuric acid, thus:

$$SO_2 + HO_2 + O \longrightarrow H_2SO_4.$$

That this really occurs can be shown by corking the flask and, after a day or two, testing the liquid with barium chloride. But the precipitate of barium sulphate is scanty, and it is plain that the production of sulphuric acid is too slow for practical purposes. *We need a catalyzer which will accelerate the process.*

Instead of corking the flask, let us hold in it a glass rod wet with nitric acid. A red gas, which is familiar to the student from his laboratory work, surrounds the rod. It is nitrogen peroxide, NO_2, and is a frequent product of chemical changes in which nitric acid takes part. The barium chloride test applied to some of the liquid in the flask now shows that a large quantity of sulphuric acid has been produced. Another portion, evaporated with a little sugar, leaves a black mass of charcoal. Conclusions:

1. Sulphur dioxide, water vapor and oxygen interact very slowly to form sulphuric acid.

2. Nitrogen peroxide is a catalyzer which enormously accelerates the change.

The way in which these facts are applied in the *lead chamber process* will be understood from a study of Fig. 84. The sulphur dioxide is made by burning pyrite, and more air than is necessary for the combustion is admitted, so that the gases leaving the furnaces still contain about 10% by volume of oxygen. They then enter the bottom of the "Glover tower," (Fig. 84*b*), which is a tower 30 ft. or more high, made of lead lined with fire brick, and packed full of little fire brick cylinders, open at both ends. Here the gases are charged with nitrogen peroxide, in a way which will be explained presently.

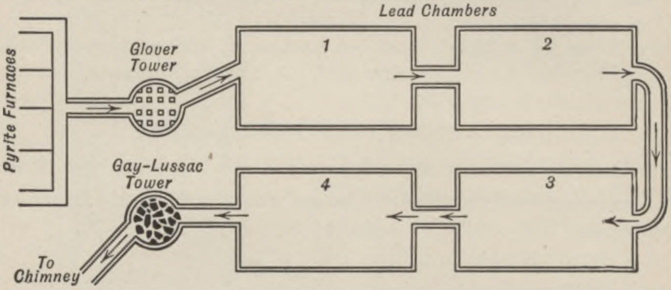


FIG. 84a.—Preparation of sulphuric acid by the lead chamber process.

They then enter the first lead chamber, where the deposition of sulphuric acid begins; the others simply continue the interaction and push it to completion. These chambers are made of thin sheet lead supported by wooden scaffolding. They are placed upon pillars, so that the bottom is accessible for repairs. A single chamber may be as much as 100 ft. long, 40 ft. wide and 40 ft. high. The water (more than the equation requires) is introduced into the chambers in a fine spray, or as steam. Short, wide lead tubes carry the gases from one chamber to the next.

The sulphuric acid falls, as a fine rain, to the bottom of the chambers. The excess of water dilutes it, so that the solution contains only about 60% of sulphuric acid. From time to time the acid is run off through tubes into a lead reservoir.

Since the action of the nitrogen peroxide is catalytic, it is not used up in the lead chambers, and since it is expensive it must be saved from the waste gases and used again. This is the important function of the "Gay-Lussac tower" (Fig. 84*c*), up through which the gases pass before they are allowed to escape. It is of lead, 30 to 60 ft. high, and is packed with coke, over which trickles concentrated sulphuric acid. This absorbs the nitrogen peroxide, so that the waste gases are almost free from it.

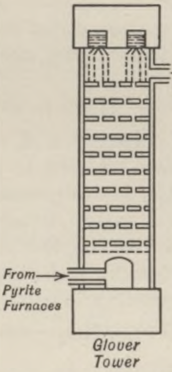


FIG. 84b.

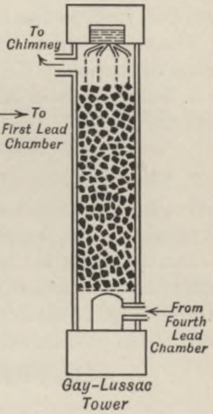


FIG. 84c.

We can now understand how the gases from the furnaces are charged with nitrogen peroxide in the Glover tower, before they enter the lead chambers. The concentrated sulphuric acid containing nitrogen peroxide—which is called "nitrose"—is pumped from the bottom of the Gay-Lussac tower to the top of the Glover and is allowed to trickle down over the little cylinders of fire brick. Through another tube, acid from the lead chambers, containing 40% of water, is run into the top of the Glover, where it mixes with the nitrose.

Nitrogen peroxide will not remain absorbed in sulphuric acid if water is added. When the acid is diluted enough to bring the percentage of H_2SO_4 down to about 70% by weight, the nitrogen peroxide bubbles out of the liquid as a gas. The 40% of water in the chamber-acid dilutes the nitrose so far that the nitrogen peroxide escapes from it and is swept into the first lead chamber. This escape takes place all the more readily, because the gases in the Glover are fresh from the furnaces and are hot (300°). Small quantities of nitric acid are run in at the top of the Glover from time to time to make up for the unavoidable losses of nitrogen peroxide.

The sulphuric acid which comes out at the bottom of the Glover is quite concentrated (over 80%), for much water has been boiled out of it in dripping over the hot cylinders of fire brick. It is ready to be pumped to the top of the Gay-Lussac tower for use in absorbing the nitrogen peroxide out of the waste gases.

Right here, then, is the foundation of the lead chamber process. From the Glover to the Gay-Lussac the nitrogen peroxide passes, through the lead chambers, doing its work of accelerating the production of sulphuric acid. In the Gay-Lussac it is dissolved in strong sulphuric acid and then pumped back to the top of the Glover where the round begins again.

The chemistry of the lead chamber process has been the subject of much discussion. We have seen that two facts are beyond question:—

1. Sulphuric acid is formed very slowly from sulphur dioxide, water and oxygen:—

$$SO_2 + H_2O + O \longrightarrow H_2SO_4.$$

2. The formation of sulphuric acid, according to the equation just given, becomes rapid if, in addition to the sulphur dioxide, water and oxygen, *nitrogen peroxide*, is also present.

The only question is as to *how* the nitrogen peroxide acts in accelerating the interaction. The simplest and most probable explanation is that sulphur dioxide, water and oxygen, interact with the nitrogen peroxide to produce sulphuric acid and *nitric oxide*:—

$$SO_2+H_2O+O+NO_2 \longrightarrow H_2SO_4+\underset{\substack{\text{nitric}\\\text{oxide}}}{NO}. \quad (1)$$

We shall see, in the next chapter, that nitric oxide instantly unites with oxygen, forming nitrogen peroxide:—

$$NO+O \longrightarrow NO_2, \qquad (2)$$

The nitrogen peroxide formed in this way at once interacts with a new portion of sulphur dioxide, water and oxygen, and forms an additional quantity of sulphuric acid, according to equation (1). According to this explanation, a trace of nitrogen peroxide could produce an unlimited quantity of sulphuric acid. In actual work, there are losses of nitrogen peroxide, which are compensated by adding nitric acid at the top of the Glover tower. Nitric acid forms nitrogen peroxide, when in contact with sulphur dioxide:—

$$SO_2+2HNO_3 \longrightarrow H_2SO_4+2NO_2,$$

so that adding nitric acid to the Glover amounts to the same thing as injecting fresh nitrogen peroxide into the lead chambers.

367. Properties of Sulphuric Acid.—Following are some of the properties of sulphuric acid:

Appearance: colorless oil.	**Specific gravity:** 1.854.
Boiling-point: 338°C.	**Familiar name:** "oil of vitriol."

Chemical properties: active acid, but less so than hydrochloric or nitric acid.

Action on plant and animal matter: blackens and destroys it; energetic caustic action on skin and clothing.

Sulphuric acid produces much heat when it comes into contact with water. This is partly due to the formation of the ions:

$$H_2SO_4 \rightleftarrows 2\overset{+}{H} + \overset{--}{SO_4}.$$

The dilute acid (ions $\overset{+}{H}$ and $\overset{--}{SO_4}$) and the concentrated acid (un-ionized molecules H_2SO_4) behave very differently, for instance:

Inter-action	*Dilute* (ions)	*Concentrated* (molecules)
Zinc	Rapid escape of hydrogen $Zn + 2\overset{+}{H} \longrightarrow \overset{++}{Zn} + H_2$, zinc sulphate is obtained when the liquid is evaporated.	No action in the cold. When heated, *hydrogen sulphide* escapes, water and zinc sulphate being produced.
Iron	Similar to zinc: $\overset{++}{Fe} + 2H \longrightarrow \overset{++}{Fe} + H_2$ Iron sulphate can be obtained from the liquid.	Hardly affects iron. Is often transported in iron tank-cars.
Copper	No action.	When heated, sulphur dioxide escapes, while copper sulphate and water are also produced.

368. Uses.—The world's annual production of sulphuric acid is about five million tons, mostly made by the lead chamber process, which yields an acid containing about 40% of water. This 60% acid is cheap and is used whenever the presence of the water is not objectionable. Thus, in the manufacture of *fertilizer* from *phosphate rock*, the powdered rock is treated with sulphuric acid. This one use takes about half the total production of sulphuric acid. Great quantities of chamber-acid are also used in making *sulphates*, especially *ammonium sulphate*, *sodium sulphate* and *aluminium sulphate*.

The industries which need an acid nearly free from water are supplied by the *contact-process*. Such acid is required in the refining of petroleum (p. 188), in the manufacture of explosives like nitroglycerin and gun cotton, and in the preparation of dye-stuffs. Sulphuric acid free from water can also be made from the chamber-acid, if conditions make it profitable to do so. All that is necessary is to heat the chamber-acid gently, until the water is evaporated. Since the boiling-point of sulphuric acid is very much higher than that of water, practically no acid escapes with the water vapor. Dishes made of fused quartz are employed to contain the chamber-acid. They are heated by the waste heat of the pyrite furnaces.

369. The Sulphates: Copper Sulphate.—"Blue vitriol" was known to the alchemists and named by them from its glassy blue crystals. For the same reason, it is often called "bluestone." The specific gravity of bluestone is 2.27. It occurs sparingly in nature, but large quantities are made artificially, for filling the kind of electric batteries used in telegraphy.

The farmer has found uses for bluestone. Seeds of wheat, rye and other grains are often moistened with a dilute solution of it before sowing. This prevents "smut," which means decay of the seed caused by fungi. The *Bordeaux mixture*, so widely used as a fungicide, is a paste, made by mixing bluestone and slaked lime.

The chemical nature of bluestone can be investigated in the following way:

1. The *barium chloride test*, applied to a solution of the crystals, shows that they consist of a sulphate.

2. When the crystals are heated in a current of hydrogen or illuminating gas, a pink mass of *copper* is left.

From (1) and (2) it follows that bluestone is *copper sulphate*.

3. By heating bluestone in a dry test tube it can be shown that the crystals contain water. Quantitative work shows

that there are five molecular weights of water to one of copper sulphate, so that the formula is $CuSO_4\ 5\,H_2O$. This water is called *water of crystallization.* Is it chemically combined, or merely mixed with the $CuSO_4$? In answering this question the student should consider that the water is present in a *definite proportion,* and that, when it is expelled by heat, the blue crystals crumble to a white powder, and show an abrupt change in all their properties.

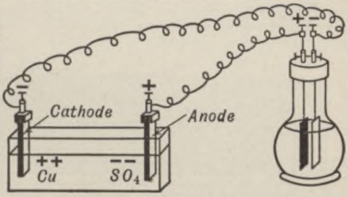


FIG. 85.—Electrolysis of copper sulphate.

370. Electrolysis of Copper Sulphate.—(*a*) When two electric light carbons, connected with the opposite poles of some source of current, Fig. 85, are dipped into a solution of copper sulphate, the negative carbon becomes coated with copper:

$$\overset{++}{\mathrm{Cu}} \longrightarrow \mathrm{Cu}.$$

At the positive carbon a gas escapes, which proves to be *oxygen.* The blue color of copper sulphate solution is due to the copper ions and disappears when they are all removed. The colorless liquid still answers to the barium-chloride test, but it tastes intensely sour and the sugar test shows that the sulphuric acid is now *free.* We may consider that the $\overset{--}{SO_4}$ ion has given up its negative charge to the positive carbon and has at once attacked a molecule of water:

$$SO_4 + H_2O \longrightarrow H_2SO_4 + O.$$

(*b*) Let us now use two weighed bits of clean sheet copper, instead of the carbons, in the electrolysis of copper sulphate solution. Copper deposits at the cathode as before, but no gas bubbles from the anode. Finally, the liquid shows no loss of color.

When the copper plates are weighed again, after the electrolysis, the cause becomes clear. *The anode has lost just as much as the cathode has gained.* For every $\overset{++}{\mathrm{Cu}}$ which gave up its charge at the cathode and became ordinary copper, a copper atom took up a charge at the anode and became an ion, $\overset{++}{\mathrm{Cu}}$. The number of copper ions in the liquid remains the same. It is as though copper had simply been transferred through the liquid, from the positive to the negative plate.

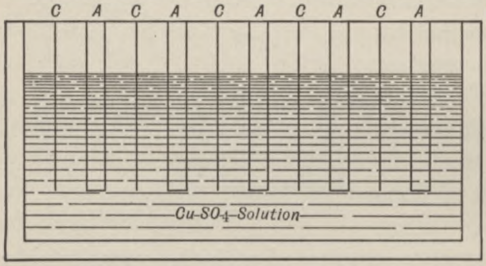


FIG. 86.—The electric refining of copper.

371. Industrial Applications.— The principle of these two experiments is applied in several important processes.

1. In **electro-plating** with copper, the object to be plated is hung in a lead-lined tank, containing a solution of copper sulphate with some free sulphuric acid, and is connected with the negative pole of a dynamo. The anode is a bar of copper. The principle is exactly the same as that of (*b*) § 370.

2. **Electrotyping** differs only in the preparation of the object. The matter is set up in type and a cast of it taken in wax. This is coated with graphite to make it conduct, and electroplated as in (1). The result is a reproduction of the original type in copper, which, owing to the graphite, is easily stripped from the wax. Lead is poured into the back of the electrotype to strengthen it and it is mounted on a wooden block. This process is used for making the plates from which books are printed. It is far too slow for newspapers.

3. On account of the large demand for pure copper to make wires for conducting the electric current, the **electric refining** of the metal is a great industry. The method is simply that of § 370 (*b*) on a large scale. The impure copper is cast into plates say 1 m. square × 2 cm. thick, which are made the anodes in a lead-lined wooden tank containing copper sulphate solution with some sulphuric acid. The cathodes are plates of pure copper 0.3 m.m. thick, Fig. 86. The liquid is kept in circulation during the process.

There are two classes of impurities in crude copper: (1) metals more active than copper, like iron and zinc—these dissolve in the bath but do not deposit on the cathode; and (2) metals less active than copper, that is, noble metals, especially gold and silver. Owing to their inactivity, these latter metals do not dissolve. They remain, coating the anode and gradually fall to the bottom of the tank, forming a *mud*. Their value is great enough to pay the whole expense of the process. With careful work the purified copper contains less than 0.01% of impurities.

372. **Zinc Sulphate.**—*Zinc sulphate*, $ZnSO_4$, is formed when zinc dissolves in sulphuric acid. It can be made by carefully roasting zinc blende:

$$ZnS + 2\,O_2 \longrightarrow ZnSO_4.$$

This method brings out clearly the difference between a sul*phide* and a sul*phate*. The sulphates of copper, iron and some other metals can also be made by oxidizing the corresponding sulphides.

Like many other salts, zinc sulphate forms several compounds with water, of which the most important is $ZnSO_4\ 7H_2O$, colorless crystals called "white vitriol." These are used in filling electric batteries, in calico-printing, and, in very dilute solution, as an eye wash.

373. **Iron Sulphate.**—*Ferrous sulphate*, $FeSO_4\ 7H_2O$, was the "green vitriol" of the alchemists, who made sulphuric acid, long before the days of the lead chambers, by heating ferrous sulphate with sand. It is obtained as a by-product from the cleaning of iron and steel castings by dipping them in dilute sulphuric acid ("pickling"). When the "pickle" is exhausted, it is heated with scrap iron and evaporated, until the ferrous sulphate separates, on cooling, in green crystals. It is used in calico-printing. Its solution is a good disinfectant for drain-pipes, for cement floors, or for anything which can be treated with it without injury. Ferrous sulphate is often called *copperas*.

374. **Ink.**—*Gallic acid* is a compound of carbon, hydrogen and oxygen closely related to pyro-gallol. It is contained in *nut galls*, and dissolves when they are powdered and treated with water. This liquid remains colorless when a solution of ferrous sulphate is added, but when the mixture is exposed

to air, oxygen is absorbed and a fine, deep black precipitate, which is the iron salt of gallic acid, appears.

This behavior is the basis of the manufacture of *ink*. A little hydrochloric acid improves the keeping qualities, and a little gum prevents the iron gallate from settling. A trace of mercuric chloride or carbolic acid is added to prevent mould. A small quantity of some greenish or bluish dye is introduced to make the writing visible when the ink is fresh.

375. Calcium Sulphate.—The mineral *gypsum* occurs in flat transparent crystals (Fig. 87), which are soft enough to be scratched with the finger-nail. A compact white form is found in extensive beds.

The orange flame color shows that gypsum is a *calcium* compound, while the barium chloride test, applied to a solution of the mineral in hydrochloric acid, proves it to be a *sulphate*. When a bit of the mineral is heated in a dry test-tube, *water* condenses in the upper part of the tube. The percentage of water can be determined by heating a weighed quantity to redness in a crucible, and weighing again. The results of this, and of other quantitative experiments, show that the formula of gypsum is $CaSO_4\ 2H_2O$.

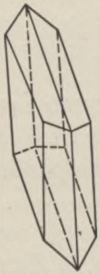


FIG. 87.—A crystal of gypsum.

376. "Plaster of Paris."—When powdered gypsum is heated to a temperature not exceeding 200°, three-fourths of the water escapes, leaving a white powder of the formula $2CaSO_4H_2O$. This is called "plaster of Paris" because it has long been made at the gypsum quarries of Montmartre, near Paris.

When water is added to plaster of Paris, the lost water is taken up again and $CaSO_42H_2O$ is again produced, as a hard, compact mass. The making of plaster casts depends upon this fact. The plaster expands a little on becoming solid and therefore gives a sharp impression of the mould. Plaster is too weak and too soluble in water to be used in out-door work.

If the gypsum is somewhat overheated, so that all the water is driven out, the plaster is spoiled, for it will not "set" with water. However, if the gypsum is thoroughly heated to bright redness (1000°), a yellowish white powder ($CaSO_4$) is formed, which, when mixed with one-third of its weight of water, slowly hardens to a stony mass.

377. **Barium Sulphate.**—*Barium sulphate*, $BaSO_4$, is the white, "insoluble" powder obtained in testing for sulphuric acid with barium chloride. 100 c.c. of water dissolves only 0.0002 gram of it, which explains why the precipitate appears, even in very dilute solutions of sulphates. It is found abundantly as the mineral *heavy spar* which often occurs with ores of lead.

Barium sulphate is often called *barytes*. It is employed as a "filler" for heavy paper, and is a frequent adulterant in paint.

378. **Potassium Sulphate.**—*Potassium sulphate,* K_2SO_4, forms colorless crystals, which contain no water. It is made at Stassfurt by mixing solutions of magnesium sulphate and potassium chloride:

$$MgSO_4 + 2\,KCl \longrightarrow MgCl_2 + K_2SO_4.$$

It is much less soluble than magnesium chloride and therefore crystallizes before the latter when the liquid is evaporated. Like potassium chloride, it is widely employed as a fertilizer, to supply potassium to plants. It is also used in making alum.

379. **Magnesium Sulphate.**—*Magnesium sulphate,* $MgSO_4$ $7H_2O$, forms colorless crystals which have long been used in medicine under the name *Epsom salt.* It is very soluble in water.

Magnesium is a grayish white metal of specific gravity 1.7 which melts at a dull red heat (750°). It is rapidly dissolved by the ordinary acids. Heated in the air, it burns, with a brilliant flame, to white *magnesium oxide,* MgO, which is often called **magnesia.** The chief use of magnesium is in making flash-light powder.

380. The Sulphates of Sodium.—Either one or both of the hydrogen atoms of sulphuric acid can be replaced by sodium. The two possible sulphates are:

Sodium hydrogen sulphate, $NaHSO_4$
Sodium sulphate, Na_2SO_4.

Sodium hydrogen sulphate can be made by treating a solution of 98 grams (one molecular weight) of sulphuric acid with 40 grams (one molecular weight) of sodium hydroxide and evaporating:

$$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O.$$

If 98 grams of sulphuric acid are mixed with a solution of 80 grams (two molecular weights) of sodium hydroxide, *sodium sulphate* is obtained on evaporation:

$$2\,NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,H_2O.$$

Sodium sulphate Na_2SO_4 is often made by treating rock salt with sulphuric acid, the mass being finally brought to a red heat:

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl.$$

Its great use is in glass-making.

The *crystals* of sodium sulphate which are formed from a water solution have the composition $Na_2SO_4\ 10\,H_2O$. Their conduct with water is a striking instance of *supersaturated solution* (p. 209). 100 c.c. of water at 20° take up from these crystals a quantity which corresponds to 20 grams of Na_2SO_4. At 34° the quantity dissolved corresponds to about 80 grams Na_2SO_4.

If the solution, saturated at 34°, is freed from all undissolved matter, it may be cooled and kept for a long time without crystallizing, but if a crystal of sodium sulphate is dropped into it, a mass of crystallized $Na_2SO_4\ 10\,H_2O$ separates at once.

381. Aluminium Sulphate.—*Aluminium sulphate,* $Al_2(SO_4)_3$, forms white crystals with $18\,H_2O$, which dissolve in about their own weight of cold water. It is often made by boiling clay (which is an aluminium compound) with sulphuric acid. More often it is made by the action of sulphuric acid upon *bauxite* which is a mineral composed of aluminium oxide and water. Bauxite occurs in Arkansas, Georgia and Alabama. The powdered mineral is boiled with chamber-acid in a great lead lined cauldron, and the solution allowed to solidify to a crystalline cake of $Al_2(SO_4)_3 18\ H_2O$.

Aluminium sulphate is an important substance. It is used in sizing paper, in making cloth water-proof, in fireproofing wood, and as a mordant in dyeing.

382. **Alum.**—We have met with many cases of the union of two elements to form a compound. Can two *compounds* do the same thing? Can they combine with each other to form a more complex compound? Compounds like $CuSO_4\ 5\ H_2O$, $ZnSO_4\ 7\ H_2O$, etc. compel us to admit that this form of combination is of frequent occurrence. We must now inquire whether two *salts* can unite to form a more complex salt which contains them both.

When a strong solution of aluminium sulphate is mixed with one of potassium sulphate, a crop of colorless octahedral crystals appears. When analyzed, these prove to contain a molecular weight of each of the sulphates·

$$K_2SO_4\ Al_2(SO_4)_3$$

and, in addition, 24 molecular weights of water. This *double salt* is called *alum.* It is used as a mordant in dyeing. Of late it has been largely displaced by aluminium sulphate, which answers the same purpose and is cheaper. Alum is still used for mordanting delicate colors because it can easily be purified, while aluminium sulphate is apt to contain a little iron, which may alter the shade. Alum is also employed in tanning glove-kid and other light leather.

The sulphates of other univalent metals form similar compounds with aluminium sulphate which are also called "alums."

Sodium alum, $Na_2SO_4\ Al_2(SO_4)_3\ 24\ H_2O$, is becoming an important salt in dyeing. Other trivalent metals like *chromium*, Cr, may take the place of the aluminium, forming salts which, though they contain no aluminium, are called alums. *Chrome alum*, $K_2SO_4\ Cr_2(SO_4)_3\ 24\ H_2O$, is a plum-colored salt. It is often added to the "hypo" fixing bath in photography, to harden the gelatin film.

The alums all crystallize in octahedra, and contain twenty-four molecules of water. They are quite numerous. Thousands of other *double salts* are known.

383. **Ammonium Sulphate.**—*Ammonium sulphate*, $(NH_4)_2SO_4$, forms colorless crystals, which dissolve in twice

their weight of water. It is made by distilling the "ammoniacal liquor" from the gas-works and coke-ovens and leading the ammonia, which escapes, into dilute sulphuric acid:

$$2\,NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4.$$

The total annual production of ammonium sulphate is nearly a million tons, and this could be greatly increased if all coke were made in ovens in which the by-products were properly collected. Its great use is as a fertilizer, to supply nitrogen to crops.

Sodium sulphite, $Na_2SO_3\ 7\,H_2O$, forms white crystals, soluble in water. Added to the developer in photography, it acts as a preservative, retarding the spoiling of the solution by absorption of oxygen. The sulphites of most metals are insoluble in water.

Sodium thiosulphate, $Na_2S_2O_3\ 5\,H_2O$, forms colorless, very soluble crystals. It is the "**hypo**" of the photographer. It is largely used in paper-making.

Related Topics

384. The Colors of Ions of the Metals.—Copper sulphate, $CuSO_4$, is white; its dilute water solution is *blue.* This color is not due to the $\overset{--}{SO_4}$ ion, for we know from the solutions of sulphuric acid, and many sulphates, that this ion is colorless. The blue color must be due to the ion $\overset{++}{Cu}$.

Copper chloride $CuCl_2$ is *brown.* Its solution in alcohol is bright grass-green and does *not* conduct the electric current, but its dilute water solution conducts and has exactly *the same blue color* as a solution of copper sulphate.

The important thing to notice here is the way the facts support the idea of ionization. Since the water solutions of copper chloride and sulphate conduct the electric current, they must contain the ion $\overset{++}{Cu}$. The identical color in the two liquids is an independent proof of the presence of the same ion $\overset{++}{Cu}$ in both.

Cobalt (Co) is a metal so similar to nickel that it is sometimes used for "nickel" plating. It is bivalent, so the ion must be $\overset{++}{Co}$.

Cobalt chloride, $CoCl_2$, is blue, and so is its alcohol solution, which is a non-conductor. The water solution conducts and has a delicate rose-pink tint. This must be the color of the $\overset{++}{Co}$ ion, for chlorine ions are colorless as we know from solutions of table-salt and of hydrochloric acid.

Cobalt nitrate is brown; the alcohol solution has the same color and does not conduct. From both facts we conclude that it contains un-ionized molecules $Co(NO_3)_2$. The water solution is a good conductor, showing that the molecules have broken into ions $\overset{++}{Co}$ and $2\overset{-}{NO_3}$, and it has *exactly the same rose color* as a water solution of cobalt chloride.

This striking difference of color between $\overset{++}{Co}$ and $CoCl_2$ is the basis of sympathetic ink. The pink dilute solution of cobalt chloride, the color of which is due to $\overset{++}{Co}$, is invisible on white paper when used as an ink. When the paper is warmed, the water is driven off and the writing appears in blue, owing to the formation of $CoCl_2$.

A rather untrustworthy way to foretell the weather can be based upon the same fact. The instrument is a rag which becomes blue for fair weather and pink for rain. The rag has been dipped in a solution of cobalt chloride. When the air is dry the water evaporates and leaves blue $CoCl_2$, but when there is much water vapor in the air (indicating rain) the $CoCl_2$ absorbs water and pink $\overset{++}{Co}$ is formed.

385. **Hydrolysis.**—We have seen (p. 256) that when hydrogen ions $\overset{+}{H}$ come into contact with hydroxyl ions $\overline{OH}$, water is instantly formed:

$$\overset{+}{H} + \overline{OH} \longrightarrow H_2O.$$

This is what really happens when an acid and a base neutralize each other.

We must now inquire whether this combination is *complete* or whether it is possible for a few $\overset{+}{H}$ and $\overline{OH}$ ions to exist together in a liquid without combination. In other words, is perfectly pure water all composed of molecules H_2O, or are there some hydrogen and hydroxyl ions scattered among the un-ionized molecules?

The plain way to get knowledge on this matter is to prepare pure water and see whether it conducts the electric current. If it does, it must contain traces of $\overset{+}{\mathrm{H}}$ and $\overline{\mathrm{OH}}$. The purest water ever obtained was made by *Kohlrausch*, by repeated distillation in a vacuum. He found that, although a very bad conductor, the water did conduct a little. Imagine a cylinder of Kohlrausch's pure water one meter long and having, as the area of its base, 1 sq. centimeter. Such a cylinder would offer about the same resistance to the current as a copper wire of the same cross-section, long enough to go around the earth at the equator 300,000 times.

From this very slight conducting power, it can be calculated that, in round numbers, there are one gram of $\overset{+}{\mathrm{H}}$ ions and 17 grams of $\overline{\mathrm{OH}}$ ions in 13 million liters of water. This may seem too small a concentration to amount to anything, but we must reflect that, owing to the smallness of the atoms, it corresponds to a very large *number* of ions. Though they are few in comparison to the un-ionized water molecules, the ions, even in pure water, are so numerous that they are only about 0.001 m.m. apart on the average. We shall see at once that this slight ionization of water into $\overset{+}{\mathrm{H}}$ and $\overline{\mathrm{OH}}$ produces some interesting results.

A solution of copper sulphate *reddens* blue litmus paper: therefore it must contain more $\overset{+}{\mathrm{H}}$ ions than pure water, which does not. Whence do these extra $\overset{+}{\mathrm{H}}$ ions come?

The water is the only possible source of them; more of it must break up into ions when copper sulphate is dissolved in it; but why?

Copper hydroxide $\mathrm{Cu(OH)_2}$ is a very *inactive base*, that is, it exists almost altogether as molecules, and hardly at all as ions $\overset{++}{\mathrm{Cu}}$ and $\overline{\mathrm{OH}}$. When copper sulphate is dissolved in water, the $\overset{++}{\mathrm{Cu}}$ ion has many $\overline{\mathrm{OH}}$ ions offered to it, and they unite to molecules $\mathrm{Cu(OH)_2}$. This cuts down the number of $\overline{\mathrm{OH}}$ ions so that there are no longer 17 grams of them in 13 million liters and more of the water molecules break up into $\overset{+}{\mathrm{H}}$ and $\overline{\mathrm{OH}}$. These new $\overline{\mathrm{OH}}$ ions unite with the $\overset{++}{\mathrm{Cu}}$ ions and so on. The $\overset{+}{\mathrm{H}}$ ions become more and more numerous, until finally there are enough of them to redden the litmus. We may say that copper sulphate solution contains a little free sulphuric acid, for it contains $\overset{+}{\mathrm{H}}$ ions from the water and $\overset{--}{\mathrm{SO_4}}$ ions from the copper sulphate.

On the contrary, a solution of sodium sulphide, Na_2S, turns red litmus *blue*. Hydrogen sulphide, H_2S, is a very *inactive acid* which exists almost wholly as un-ionized molecules when dissolved in water. When sodium sulphide is dissolved it separates into $2\overset{+}{\mathrm{Na}}$ and $\overset{--}{\mathrm{S}}$. The sulphur ion $\overset{--}{\mathrm{S}}$ finds numerous $\overset{+}{\mathrm{H}}$ ions ready to unite with it and H_2S molecules are formed. The $\overline{\mathrm{OH}}$ ions, which are left, become abundant enough to turn the red litmus blue.

A solution of table-salt has no effect on either red or blue litmus. Both sodium hydroxide and hydrochloric acid are very active, that is, almost completely ionized. Hence there is no union either of $\overset{+}{\mathrm{Na}}$ and $\overline{\mathrm{OH}}$ or of $\overset{+}{\mathrm{H}}$ and $\overline{\mathrm{Cl}}$ and the number of $\overset{+}{\mathrm{H}}$ and $\overline{\mathrm{OH}}$ ions remains the same as in the pure water.

These are merely examples. It may be left as an exercise to the student to show from them that:

(1) A salt of an active acid with an inactive base will redden blue litmus. Examples: copper sulphate, chloride and nitrate, aluminium sulphate.

(2) A salt of an active base with an inactive acid will turn red litmus blue. Examples: sodium sulphide, sodium cyanide (p. 210), washing-soda (sodium carbonate), borax (sodium borate).

(3) A salt of an active acid with an active base will not change the color of either kind of litmus. Examples: sodium chloride, nitrate and sulphate and the same salts of potassium and calcium. All these instances can be quickly tested in the laboratory.

(4) The chemical equation for the hydrolysis of a salt is merely the equation for the neutralization of the corresponding acid and base, read backward. **Hydrolysis is the reverse of neutralization.**

386. Electrolysis of Water.—When water is placed in the apparatus of Fig. 88, and the electric circuit completed, no gas escapes at either electrode because the resistance of the water is so great that hardly any current passes. But if a little sodium sulphate, Na_2SO_4, is dissolved in the water the current passes at once: oxygen escapes at the anode and twice as much hydrogen by volume at the cathode.

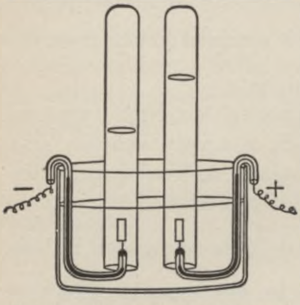


FIG. 88.—The electrolysis of water.

The current did not pass through the water, because there were not enough ions to carry it. It does pass through the sodium sulphate solution, because the innumerable $\overset{+}{Na}$ ions carry the positive electricity to the cathode while the $\overset{--}{SO_4}$ ions carry the negative electricity to the anode. So much is clear.

But what happens at the cathode? Hitherto we have assumed in such cases (p. 244) that the sodium ion gives up its charge and is changed for an instant into sodium metal, which interacts with water:

$$Na + H_2O \longrightarrow NaOH + H \qquad (1)$$

That view served a good purpose as a beginning. We want now to penetrate more deeply into the matter.

Is there any proof that sodium ions are discharged at all? A crowd of positive ions is pulled to the cathode by its negative charge. This crowd consists mainly of sodium ions, but there are millions of hydrogen ions in it from the water. The hydrogen ions lose their charges far more easily than the sodium ions, so they give up their positive electricity to the cathode and form hydrogen gas:

$$2\overset{+}{H} \longrightarrow H_2$$

The part played by the sodium ions is merely to carry the positive electricity through the liquid.

The same fact holds true for the anode. The work of carrying the negative electricity to it is done mainly by the $\overset{--}{SO_4}$ ions, but in the army of negative ions which are drawn to the anode are multitudes of hydroxyl ions $\overline{\text{OH}}$, from the water. These lose their negative electricity much more easily than the $\overset{-\,-}{\text{SO}_4}$ ions so they *do* lose it, and oxygen escapes:

$$2\,\overline{\text{OH}} \longrightarrow \text{H}_2\text{O} + \text{O}$$

As the electrolysis goes on, fresh molecules of water are always breaking up into $\overset{+}{\text{H}}$ and $\overline{\text{OH}}$ so that the concentration of both always remains the same.

As this experiment is commonly carried out on the lecture table, *sulphuric acid*, instead of sodium sulphate, is added to the water. The result at the anode is exactly the same as when sodium sulphate is used. At the cathode, matters are still simpler. Multitudes of $\overset{+}{\text{H}}$ ions collect there, are discharged and converted into hydrogen gas. It makes no difference whether they come from the water, or from the acid.

387. The Electromotive Series of the Metals.—When a strip of zinc is placed in a solution of copper sulphate, or any other soluble copper salt, a red deposit of *copper* is produced upon the zinc. At the same time, zinc dissolves:

$$\text{CuSO}_4 + \text{Zn} \longrightarrow \text{ZnSO}_4 + \text{Cu}$$

$$\text{or, better, } \underset{\text{Copper ion}}{\overset{++}{\text{Cu}}} + \underset{\text{zinc metal}}{\text{Zn}} \longrightarrow \underset{\text{copper metal}}{\text{Cu}} + \underset{\text{zinc ion}}{\overset{++}{\text{Zn}}}$$

A strip of *silver*, however, is *not* coated with copper when dipped into a solution containing copper ions. On the contrary, when copper is placed in a solution containing silver ions, *silver* is deposited upon the copper. Since silver is univalent, the equation is:

$$\underset{\text{Silver ion}}{2\,\overset{+}{\text{Ag}}} + \underset{\text{Copper metal}}{\text{Cu}} \longrightarrow \underset{\text{Silver metal}}{2\,\text{Ag}} + \underset{\text{Copper ion}}{\overset{++}{\text{Cu}}}$$

Zinc, placed in a solution containing silver ions, becomes coated with *silver*:

$$\underset{\text{Silver ion}}{2\,\overset{+}{\text{Ag}}} + \underset{\text{Zinc metal}}{\text{Zn}} \longrightarrow \underset{\text{Silver metal}}{2\,\text{Ag}} + \underset{\text{Zinc ion}}{\overset{++}{\text{Zn}}}$$

Thus, if we arrange these three metals in the following order:

Zinc
Copper
Silver

we can say that each metal *precipitates* those which follow it and *is precipitated* by those which precede it. When all of the important metals are included in an investigation of this sort, the resulting arrangement is known as the *electromotive series*. It is as follows:

The Sodium Group
The Calcium Group
Magnesium
Aluminium
Manganese
Zinc
Chromium
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
HYDROGEN
Copper
Antimony
Bismuth
Mercury
Silver
Platinum
Gold

Any metal in this series will precipitate *metal* from a solution containing *ions* of any of the metals which follow it, but will not affect a solution containing ions of a metal preceding it. The metals preceding *hydrogen* liberate hydrogen gas from solutions containing hydrogen ions, that is from *acids;* those which follow hydrogen do not. Since *water itself* contains hydrogen ions, the metals preceding hydrogen *rust* in contact with water, and, for this reason, are hardly found in the free state in nature: those following hydrogen scarcely rust and are therefore found native, although most of them also occur as compounds. The student will note that chemical activity decreases as we descend the table, the sodium group being intensely active, while platinum and gold are the most inert of the metals.

We have seen that galvanized iron resists the action of the weather much better than iron plated with tin. The electromotive series explains this fact. Since zinc precedes iron, water will have no action upon the iron until the zinc has all rusted. On the other hand, iron precedes tin and therefore the iron rusts first when iron and tin are exposed together to water. Hence the protection afforded by tin against rusting lasts only as long as the plating of tin over the iron remains unperforated.

Definitions

Anhydride. An oxide which combines with water, producing an acid.

Hydrolysis. The interaction of a *salt* with *water,* producing an *acid* and a *base.* Hydrolysis is merely the *reverse* of neutralization.

CHAPTER XXIII

NITRIC ACID AND ITS SALTS.—COMPOUNDS OF NITROGEN AND OXYGEN.—CHLORIC ACID AND ITS SALTS

388. **Chili Saltpeter.**—In the province of *Tarapaca*, which occupies the almost rainless part of northern Chili, between the Andes and the Pacific, are found great beds of a mineral called *Chili saltpeter.*

When pure, the mineral forms transparent, colorless crystals, very soluble in water, but it is commonly found in masses colored gray, brown or yellow. That it is a *sodium* compound is clear from the intense yellow which it gives to the flame. When some of the mineral is heated in a glass tube it gives off a gas which the spark test shows to be *oxygen.* When the powdered mineral is mixed with about ten times its volume of iron powder, and heated, a gas escapes which can be collected over water, and shown to be *nitrogen.* Finally, if the mineral is gently warmed with a little sulphuric acid, a vapor escapes which, when condensed to a liquid, proves to be *nitric acid,* HNO_3. Chili saltpeter is the sodium salt of nitric acid; it is *sodium nitrate,* $NaNO_3$.

389. **The Production of Sodium Nitrate.**—In Chili, the crude mineral is treated with boiling water in iron boxes, and the solution of the sodium nitrate, freed from insoluble impurities, is allowed to crystallize. This product, which contains about 95% of sodium nitrate, is shipped to the United States and to Europe. Considerably more than a billion dollars worth of sodium nitrate has been obtained from the Tarapaca beds, and it is claimed that enough remains to supply the demand for two centuries or more. It is being exported at the rate of nearly two million tons a year. Much of it goes on the soil, as a nitrogen fertilizer, and the rest chiefly into the manufacture of nitric acid

390. Nitric Acid: Preparation.—*Nitric acid,* HNO_3, is made by gently heating sodium nitrate with sulphuric acid:

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

The mixture is contained in a horizontal iron cylinder (Fig. 89), which will take about five tons of the nitrate, and rather more than that quantity of sulphuric acid (chamber-acid). The vapor is condensed in a series of stoneware bottles.

Any nitrate will yield nitric acid with sulphuric acid. Sodium nitrate is used because it is cheap. Sulphuric acid is chosen for the same reason, and also on account of its high boiling-point. When sulphuric acid and sodium nitrate are mixed in the cold, there is a partial interaction: sodium hydrogen sulphate and nitric acid are formed, until their concentration becomes great enough to prevent the change from going any further. But when heat is applied, the nitric acid is removed, as vapor, so that its concentration is kept below the limiting value, and the change goes on to completion. Taking into account that sulphuric acid boils at 338° and nitric acid at 86°, could sulphuric acid be made by distilling sodium hydrogen sulphate with nitric acid?

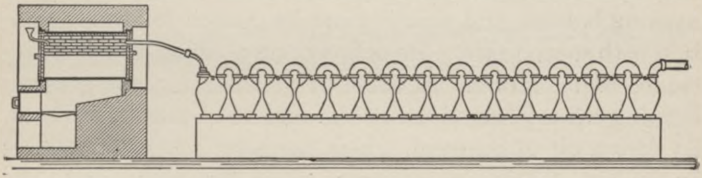


FIG. 89.—The manufacture of nitric acid.

391. Properties of Nitric Acid.—Pure nitric acid is a colorless liquid about one and a half times as heavy as water. It boils at 86° and freezes at −50°. The concentrated nitric acid of the laboratory contains 68% of HNO_3, the rest being water, which reduces its specific gravity to 1.41.

The student has probably noticed that the nitric acid in the bottles which stand near the windows, in strong light, is red. Some of the acid is decomposed by light:

$$2\,HNO_3 \longrightarrow H_2O + 2\,NO_2 + O$$

and the nitrogen peroxide dissolves in the rest and colors it. The same decomposition occurs when the acid is heated, and gives some trouble in its manufacture.

Nitric acid is evidently an unstable substance. The formula HNO_3 shows that it contains $\frac{48}{63}$ of its weight of oxygen, which is more than three-fourths. Putting these two facts together, it is reasonable to expect that the acid will prove to be a violent oxidizing agent, for all this loosely held oxygen will be offered freely to any substance which will accept it. There are 800 liters of oxygen in a liter of pure nitric acid.

It is not surprising, therefore, that nitric acid may set fire to the hay, straw and sawdust which are often used in packing bottles, and that it must be packed for transportation with special care. Its action upon clothing is another instance of oxidation. A flame of illuminating gas goes on burning when plunged under the surface of pure nitric acid. So does a bit of charcoal, which has been heated to redness in the air. The warm vapor of nitric acid responds to the spark test.

Nitric acid is one of the most active acids known. The name which the alchemists gave to it, *aqua fortis*, refers to this fact. Its behavior with bases is similar to that of hydrochloric acid and has already been briefly discussed.

392. Action of Nitric Acid on Metals.—Nitric acid does not affect platinum or gold. Most of the other familiar metals, like iron, zinc, copper, lead, silver and mercury, are rapidly dissolved as nitrates. The last four are hardly attacked by hydrochloric or dilute sulphuric acid.

The equations for the interaction of nitric acid with metals are difficult to write. This is because the acid acts not only as an *acid*, but also as an *oxidizing agent*. The essential thing about the interaction of an acid and a metal is that hydrogen escapes and the atom of the metal is taken into the solution instead. In the case of nitric acid, however, this hydrogen does *not* escape. It is oxidized to water by another molecule of nitric acid and this action produces complications, as can be seen from an example: Zinc is rapidly converted into zinc nitrate, $Zn(NO_3)_2$, by moderately concentrated nitric acid, but no hydrogen escapes—the gas given off is red nitrogen peroxide NO_2. We may assume that, for an instant, hydrogen is liberated as usual:

$$Zn + 2\,HNO_3 \longrightarrow Zn(NO_3)_2 + 2\,H \qquad (1)$$

but is oxidized at once by more nitric acid:

$$H + HNO_3 \longrightarrow H_2O + NO_2 \qquad (2)$$

If the nitric acid is diluted with five times its volume of water, zinc nitrate is formed as before (1) but no nitrogen peroxide escapes. The gas formed is colorless nitric oxide, NO. Three atoms of hydrogen have attacked one molecule of nitric acid:

$$3\,H + HNO_3 \longrightarrow 2\,H_2O + NO \qquad (3)$$

Nitric oxide also escapes when copper dissolves in dilute nitric acid, the equations being similar to (1) and (3).

The two steps can be combined in one equation, which may be needed in solving numerical problems. When copper dissolves in nitric acid we have:

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

In the case of tin, and some other substances, the acid acts chiefly as an oxidizing agent. The product, when dried by heat, consists of tin dioxide:

$$Sn + 4\,HNO_3 \longrightarrow SnO_2 + 2\,H_2O + 4\,NO_2.$$

393. **Uses of Nitric Acid.**—Nitric acid is made in large and increasing quantities. The chief use of the concentrated acid is in the manufacture of high explosives, like nitroglycerine and guncotton (Chap. XXVIII). The dilute acid is used in the preparation of the copper-plates from which etchings are printed, in making silver nitrate, ammonium nitrate and other nitrates, and in dissolving metals. From an alloy of gold and silver not too rich in gold, it dissolves out the silver, leaving the gold. It was formerly used in mints for the separation of these two metals, but hot concentrated sulphuric acid, which acts in the same way and which is cheaper, displaced it. The separation of gold and silver in mints is now

carried out by an electrical method, similar in principle to the refining of copper.

394. **The Nascent State.**—We have just seen that hydrogen, generated in a liquid containing nitric acid, is not permitted to escape, but is oxidized to water. But if the hydrogen is made in another vessel and passed into dilute nitric acid through a glass tube, it bubbles through the liquid without change.

If silver chloride, $AgCl$, is suspended in water and hydrogen is passed into the water there is no effect, but if zinc and hydrochloric acid, or any mixture which can generate hydrogen, are added to the *same* liquid, the silver chloride is rapidly converted into metal:

$$AgCl + H \longrightarrow HCl + Ag$$

It seems from these, and many similar instances, that hydrogen, at the instant of its liberation, before it has taken form at all as a gas, is *more active* than hydrogen gas already formed.

The atomic theory suggests, as an explanation, that the hydrogen is first liberated as single atoms. When these unite to form the molecules H_2 of hydrogen gas, they become less active, because the bond between the two must be ruptured before any chemical action can occur. Perhaps the chief value of such a hypothetical explanation is that it helps us to remember the *fact* that not only hydrogen but many other elements are more active in the moment of production—in the **nascent state**, as it is called—than they are afterward.

Some powdered metals, like platinum, absorb hundreds of times their volume of hydrogen and these solid solutions are able to produce many of the effects of nascent hydrogen. This fact is in direct conflict with the above explanation. In these cases, the greater activity is clearly due to the greater *concentration* of the hydrogen.

395. **Aqua Regia.**—A mixture of nitric and hydrochloric acid is called *aqua regia*. It dissolves gold and platinum, which are not acted upon by either acid singly. The reason is that the nitric acid oxidizes the hydrogen of the hydrochloric acid to water, liberating chlorine. The nascent chlorine converts the metal into chloride, which dissolves.

396. **Salts of Nitric Acid.**—The formula of nitric acid shows that the radical NO_3 is univalent. Hence the formulas of the nitrates can be written at once if the valence of the metal is known. Some examples will make this clear. The only unfamiliar substance in the list is *thorium nitrate*,

which is a white solid, much used in making Welsbach mantles.

Metal	*Valence*	*Formula of Nitrate*
Potassium	1	KNO_3
Calcium	2	$Ca(NO_3)_2$
Aluminium	3	$Al(NO_3)_3$
Thorium	4	$Th(NO_3)_4$

The nitrates are all freely soluble in water. The ion $\overline{NO_3}$ is colorless.

397. Potassium Nitrate.—*Potassium nitrate*, KNO_3, is commonly called "nitre," or "saltpeter." It forms colorless prisms which contain no water of crystallization. To make it, Chili saltpeter and Stassfurt potassium chloride are placed, with a limited quantity of water, in a steam-heated iron vessel:

$$NaNO_3 + KCl \longrightarrow KNO_3 + NaCl$$

In an hour, most of the sodium chloride has separated, and the liquid is filtered through canvas to remove it. When the liquid is allowed to cool in another tank, the potassium nitrate crystallizes.

The principle of the method will be clear from a glance at the solubility curves of table-salt and nitre (Fig. 74). The solubility of table-salt is scarcely increased by heat, and it separates in the hot liquid because there is not enough water present to dissolve it. The nitre remains dissolved so long as the liquid is hot, because of its great solubility at higher temperatures, but crystallizes on cooling, on account of the great reduction in its solubility.

398. Black Gunpowder.—Potassium nitrate finds its main use in the manufacture of black gunpowder. This is a mixture containing, by weight, about 6 parts potassium nitrate, 1 part charcoal, and 1 part sulphur. The materials are finely powdered separately, mixed, and granulated. It is still largely used for hunting and saluting. In warfare, it is obsolete.

We may write a simplified equation for the explosion of gunpowder:

$$2\,KNO_3 + 3\,C + S \longrightarrow K_2S + 3\,CO_2 + N_2$$

The chemistry of the explosion is really quite complicated, but this simple equation will help us to remember that the nitre serves as a source of oxygen to burn the carbon, and that the nitrogen escapes as gas. In fact, the sudden formation of gas is really the cause of the explosion. The gases from 1 c.c. of powder would occupy, at S.T.P., about 500 c.c. and this volume is vastly increased by expansion, due to the high temperature. Since this sudden expansion requires only a small fraction of a second, the reason for the effects of the explosion is plain.

It would be a mistake to conclude from these effects that gunpowder contains *more energy* than ordinary fuels, for the direct reverse of this is true. One gram of gunpowder when burned yields about 600 cal., while one gram of the best coal gives about 8000 cal. Hence if warships were driven by engines which burned gunpowder, their fuel-bunkers would have to be made more than a dozen times as large as at present. The point is not that so *much* energy is evolved in the explosion of gunpowder, but that energy is evolved so *quickly*.

399. **Silver Nitrate.**—*Silver nitrate*, $AgNO_3$, forms flat colorless crystals, very soluble in water. It is made by dissolving silver in nitric acid. When heated, the crystals melt and, at a higher temperature, decompose, leaving a residue of silver.

When silver nitrate gets upon the hands, the organic matter of the skin converts it into silver, which produces a black stain. The same action occurs in linen or cotton goods, so that a solution of silver nitrate is used as **indelible marking-ink.** Silver nitrate is employed in medicine as "**caustic**" for the removal of warts, etc. Its chief use is in the manufacture of photographic plates and films (p. 269).

400. **Ammonium Nitrate.**—*Ammonium nitrate*, NH_4NO_3, forms colorless crystals very soluble in water. If the water is stirred with a thermometer, it is found that the dissolving of the ammonium nitrate is accompanied by a decided fall in temperature. If the beaker is stood upon a wet block of wood, while the ammonium nitrate is dissolving, the block will be frozen to the bottom of the beaker.

As a rule, although there are marked exceptions, the formation of solutions of solids in liquids *absorbs* heat.

Ammonium nitrate is made by distilling the ammonia-liquor obtained as a by-product of coke-ovens and gas-works, and leading the ammonia gas which escapes into nitric acid:

$$NH_3 + HNO_3 \longrightarrow NH_4\ NO_3.$$

The fire-damp (p. 181), which causes so many accidents in soft-coal mines, can be ignited not only by the flames of the miners' lamps, but also by the blasting necessary to bring down the coal. The main use of ammonium nitrate is in the manufacture of "safety explosives," that is explosives which are not likely to ignite fire-damp. Explosives of this sort are often made by mixing powdered ammonium nitrate with combustible substances like naphthalene, rosin, sulphur or even flour. They also possess the great advantage of not being sensitive to shock, so that they can be handled and transported without danger.

401. Nitrous Oxide.—When ammonium nitrate is heated it first melts and then decomposes:

$$NH_4NO_3 \longrightarrow 2\,H_2O + \underset{\substack{\text{nitrous}\\\text{oxide}}}{N_2O}$$

Nitrous oxide is a colorless gas, which dissolves in about its own volume of water at room temperature. Like all gases, it is less soluble in hot water. Priestley discovered it, and Sir Humphry Davy found that, when inhaled, a little produced intoxication (hence the name, "laughing gas"), while more caused the subject to become insensible for a short time. This latter effect has caused it to be widely used by dentists, who purchase it liquefied in steel cylinders.

Like oxygen, nitrous oxide gives the spark test. Unlike oxygen, nitrous oxide does not unite completely with substances which are burned in it. A volume of *nitrogen* equal to that of the nitrous oxide is left.

The nitrous oxide required to fill our standard cube of 22.4 liters at S.T.P. weighs 44 grams. Let all the oxygen be removed, from this amount of the gas, say by burning iron to iron oxide in the gas. Then 22.4 liters of nitrogen will remain which will weigh (p. 109) 28 grams or two atomic weights (N_2). The 16 grams of oxygen which have combined with iron represent one atomic weight (O). Hence the formula is N_2O.

402. Nitric Oxide.—*Nitric oxide,* NO, may be made by dissolving copper in dilute nitric acid. It is a colorless, poisonous gas, slightly soluble in water. The oxygen is more firmly held in it than in nitrous oxide, as can be seen by comparing the behavior of the two gases toward combustible substances:

Combustible	*Nitrous Oxide*	*Nitric Oxide*
Splinter bearing sparks	bursts into flame	extinguished
Burning candle	burns with increased energy	extinguished
Sulphur burning feebly	extinguished	extinguished
Sulphur burning freely	burns with increased energy	extinguished
Phosphorus burning feebly	burns with increased energy	extinguished
Phosphorus burning freely	burns with increased energy	burns energetically
Burning magnesium	burns with increased energy	burns energetically

After combustions with nitric oxide, a volume of nitrogen equal to one-half that of the nitric oxide is left.

22.4 liters of nitric oxide weigh 30 grams. After the oxygen has all been removed by heated iron, 11.2 liters of nitrogen remain, which weigh 14 grams or one atomic weight (N). The 16 grams of oxygen which have combined with iron represent one atomic weight (O). Hence the formula is NO.

403. Nitrogen Peroxide.—When a bottle filled with nitric oxide is opened, the gas at once becomes deep reddish brown. This is owing to the formation of nitrogen peroxide:

$$NO + O \longrightarrow \underset{\substack{\text{nitrogen}\\\text{peroxide}}}{NO_2}$$

The injurious action of nitric oxide is therefore really due to nitrogen peroxide, which is formed as soon as nitric oxide meets the air.

Nitrogen peroxide is a poisonous gas and is all the more dangerous because the first effects are not very noticeable. For this reason the red gas given off when nitric acid acts upon metals should not be inhaled. Nitrogen peroxide disappears when shaken with water, but not by mere solution. A chemical change takes place and nitric acid and nitric oxide are formed:

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$

Nitrogen peroxide supports combustion brilliantly, for its oxygen is abundant and loosely held.

404. **Sodium Nitrite.**—When sodium nitrate is carefully heated one-third of the oxygen escapes:

$$\underset{\substack{\text{sodium}\\ \text{nitrate}}}{NaNO_3} \longrightarrow \underset{\substack{\text{sodium}\\ \text{nitrite}}}{NaNO_2} + O$$

Sodium nitrite is made by melting sodium nitrate with lead in cast-iron kettles.

$$NaNO_3 + Pb \longrightarrow NaNO_2 + PbO$$

Since the lead oxide is insoluble and the sodium nitrite very soluble in water, they are easily separated. The lead oxide is made into red lead (p. 78).

Most of the metals form nitrites. Sodium nitrite, which forms pale yellow crystals, is the only one of commercial importance. It is much used in the manufacture of dyes. It is now obtained in Norway as a by-product, in the production of nitric acid from the air (p. 307).

405. **Potassium Chlorate.**—*Potassium chlorate*, $KClO_3$, is the white salt used in the laboratory in making oxygen. It is made by passing the electric current through a solution of potassium chloride, which is stirred constantly:

$$KCl + 3\,H_2O \longrightarrow KClO_3 + 3\,H_2$$

The change takes place in several stages and the equation merely sums up the final result.

Potassium chlorate forms flat white crystals which contain no water of crystallization. 100 c.c. water dissolves at 0°, 3 grams and, at 100°, 60 grams.

The oxygen of potassium chlorate is loosely held. A mixture of the salt with red phosphorus (Chap. XXV) explodes violently when struck. A crystal of potassium chlorate, when ground in a mortar with a little sulphur, produces a series of explosions. The signal caps used on railroads consist of a mixture of sulphur and potassium chlorate contained in a small tin box shaped like a blacking box. A flexible wire made of lead is attached to the box for fastening it to the rail.

Potassium chlorate is used in the preparation of dyestuffs, explosives and safety matches. Its solution is excellent as a gargle for an inflamed throat, but, since potassium chlorate is poisonous, the liquid must not be swallowed.

Sodium chlorate, $NaClO_3$, is a white salt which finds similar applications.

Chloric acid, $HClO_3$, is a colorless explosive liquid, which sets fire to paper and other combustibles.

Related Topics

406. Converting the Nitrogen of the Air into Useful Compounds.—Over a million tons of sodium nitrate are used as a fertilizer each year, purely on account of the nitrogen which the salt contains, yet the leaves, and even the roots, of the plants to which the nitrate is applied are surrounded by *air* which contains four fifths of its volume of nitrogen. Thus the farmer pays a high price for the very element which blows about by the cubic mile over his fields.

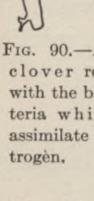


FIG. 90.—A clover root with the bacteria which assimilate nitrogen.

The reason is that *most plants cannot take up free nitrogen*. They must have it supplied as a nitrate. Plants can utilize ammonium compounds, because the nitrogen is easily oxidized to nitrates in the soil, but free nitrogen is useless to them.

A few plants are exceptions. Clover thrives on soils which, because the nitrates are exhausted, are barren to most crops. On the roots of the clover are found small lumps which contain numbers of a peculiar species of rather large bacteria (Fig. 90). These oxidize the nitrogen of the air which

JUSTUS VON LIEBIG

B. Germany, 1803. D. Munich, 1873.

Founded agricultural chemistry. First pointed out the necessity of fertilizing the soil and showed how to prepare fertilizers. Investigated the chemistry of nutrition in the animal body. Studied fermentation. First prepared pure antimony. Invented the "potash bulb" (p. 100).

bathes the roots to nitrates. The nitrates are then absorbed by the plant.

However, most crops do not share this power of clover, and the problem of converting the nitrogen of the air into some compound, which can serve as nourishment for them, is one which increases in importance, as the sodium nitrate supply of Chili approaches exhaustion. The air over a nine-acre field contains as much nitrogen as the present annual product of the Chilian beds.

407. Making Nitric Acid from Air.—The *production of nitric acid from the air* is carried out in three stages:

1. The nitrogen and oxygen of the air are combined to nitric oxide:

$$N + O \longrightarrow NO$$

2. The nitric oxide is allowed to unite with more oxygen:

$$NO + O \longrightarrow \underset{\text{nitrogen peroxide}}{NO_2}$$

3. The nitrogen peroxide is made to interact with water:

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO.$$

(2) and (3) have been briefly discussed (p. 304), but we have yet to learn the methods used on the large scale.

1. Whenever air is intensely heated, partial union of the nitrogen and oxygen, to form nitric oxide, takes place. The most effective method of heating is the electric arc and, around an ordinary arc lamp, traces of nitric oxide are formed. But if the air is allowed to cool slowly, after passing through the arc, all the nitric oxide will separate into its elements during the cooling. The problem, then, is to heat large volumes of air by means of an arc, and to provide that the air is *suddenly* cooled, so that the nitric oxide has no chance to decompose.

The inside of the furnace in which the arc is formed is shaped like a very flat drum standing on its edge. That is to say, it is circular, 2 meters wide, 2 meters high and only a few centimeters thick (Fig. 91). Through the *narrow* walls which form the edges of the drum project the electrodes between which the arc is to burn. They are made of copper and are hollow, so that they can be cooled by water circulating in the interior. They approach each other closely in the center of the circle, only one centimeter separating them.

Strong electro-magnets placed close to the center of the circle, but outside the furnace, broaden out the arc into a great disc of flame, like an electrical sun, which fills the inside of the furnace. The air is forced in at the top and air containing 1% by volume of nitric oxide, and having a temperature of 700°, leaves the furnace at the bottom.

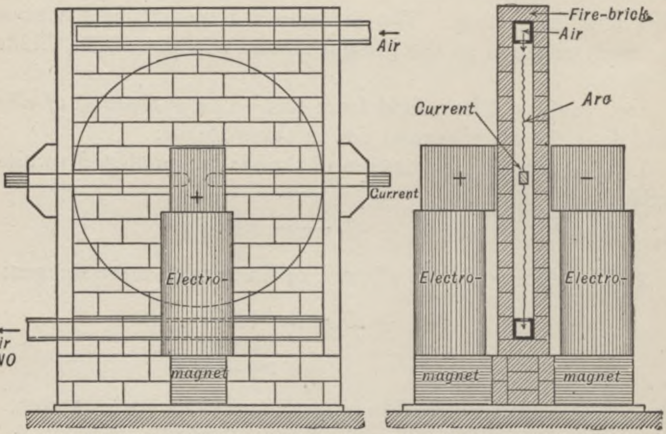


Fig. 91.—Preparation of nitric acid from air.

2. Since the gases leaving the electric furnace still contain much oxygen, nitrogen peroxide will be formed from the nitric oxide as soon as the gases are cool enough to allow it. They are passed up into large towers built of iron where the nitric oxide unites with oxygen.

3. The air, which now contains about 1% by volume of nitrogen peroxide, is then passed in at the bottom of a granite tower filled with quartz pebbles, over which water trickles. Here the nitrogen peroxide interacts with the water, forming nitric acid. Several such towers are in use. By allowing the water to trickle through repeatedly, the percentage of nitric acid in it may be raised to fifty. The nitric acid is converted into *calcium nitrate*, $Ca(NO_3)_2$, which contains 13% of nitrogen, and

finds ready sale as a fertilizer. It has some advantages over Chili saltpeter and can be sold at a price to compete with it. The factory is situated at Notodden, Norway, where there is abundant water power to generate the electric current. It is a complete industrial success.

Another type of electric furnace can be used to bring about the combination of the nitrogen and oxygen to nitric oxide in the first stage. This consists of a long iron tube in which an arc 5 meters long burns, between electrodes at top and bottom (Fig. 92). The air is forced in at the bottom through a side-tube which has the direction of a tangent to the surface of the main tube. The result is that the air acquires a whirling motion which keeps the arc in the center where the motion is least. The long thin arc is really a flame of nitrogen burning to nitric oxide, 2% of which is contained in the gas which passes out at the top. It is converted into nitrogen peroxide and nitric acid as described above.

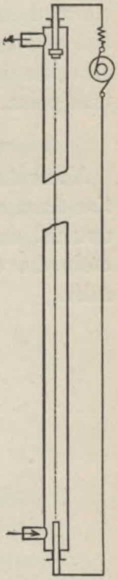


FIG. 92.—Another furnace for making nitric acid from air.

408. "Nitro-lime" from the Air.—When *calcium carbide*, CaC_2, is heated in a current of nitrogen a substance whose commercial name is *nitro-lime* is formed:

$$CaC_2 + N_2 \longrightarrow \underset{\text{nitro-lime}}{CaCN_2} + C$$

The nitrogen is made from the air by Linde's method (p. 176). Air is liquefied and allowed to trickle down a tower filled with glass balls. Nitrogen gas, nearly pure, escapes at the top, while liquid oxygen collects at the bottom. This cheap and almost complete separation is due to the fact that nitrogen has a lower boiling-point than oxygen: oxygen condenses at a higher temperature.

When the tower is working, the bottom contains liquid oxygen from the surface of which oxygen gas escapes and ascends among the glass balls. But it does not get very far for, trickling over them, it meets liquid nitrogen, whose temperature (–194°) is lower than the point at which oxygen condenses (–183°). Hence the oxygen becomes liquid and flows down, while an equivalent amount of nitrogen becomes a gas and moves upward. We have seen (p. 177) that this is the only method by which oxygen is now made on a large scale.

The nitrogen which escapes from the top of the tower is led into numerous small furnaces, filled with calcium carbide, and heated to redness electrically. Here nitrogen is absorbed and nitro-lime formed.

Nitro-lime, $CaCN_2$, is a hard gray-black mass resembling compact coke. As the formula shows, it is rich in nitrogen. It is claimed that the nitrogen is rapidly oxidized to nitrates in the soil and that nitro-lime is an excellent fertilizer, but agricultural chemists do not seem to have reached an agreement on this important point.

Definition

Nascent state. The state of an element at the instant of its *liberation* from a compound. The nascent state is characterized by an unusual chemical *activity*, which may be due to the fact that the *atoms* have not yet had time to unite with each other to form *molecules*.

CHAPTER XXIV

THE CARBONATES: BLEACHING POWDER, HYDROGEN PEROXIDE, OZONE

409. Calcite.—When a broken piece of marble is examined it is seen to resemble loaf-sugar in structure. It is composed of crowded crystals which have had no space to develop. These are composed of a mineral called *calcite.*

Under more favorable circumstances, calcite forms large, colorless, transparent crystals which are found in various forms, one of which is shown in Fig. 93. The same figure illustrates the power of the crystal to split light passing through it into two rays, which take different directions, so that objects seen through it appear double. This property is called **double refraction** and is utilized in optical apparatus.

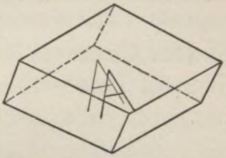


FIG. 93.—A crystal of calcite.

410. The Metal of Calcite.—When a bit of calcite is held in the flame, the orange color which appears proves that we are dealing with a *calcium compound* (p. 262). The color is more intense if the mineral is moistened beforehand with hydrochloric acid.

Calcium is made from calcium chloride, $CaCl_2$, which is obtained by dissolving calcite in hydrochloric acid, evaporating, and drying the residue by heat. The calcium chloride is melted in a graphite crucible, which forms the anode of the electric current. The cathode is an iron rod which at first dips into the melt. Chlorine escapes at the anode, and calcium separates and clings to the cathode. Later the iron rod, acting as cathode, is gradually raised out of the liquid, so that the calcium itself serves as cathode, and a lengthening rod of it is formed. Calcium is now made very cheaply by this process, and no doubt important uses will be found for it.

411. Calcium—Some information concerning calcium is summarized in the following table:

Symbol: Ca.
Atomic weight: 40.
Specific gravity: 1.61 (very light therefore).
Melting-point: 760°.
Chemical conduct: active but less so than sodium.
Behavior towards oxygen: burns brilliantly to calcium oxide CaO (lime).
Behavior toward moist air: Rusts rapidly, must be kept in sealed bottles.

When calcium is thrown into the water, hydrogen escapes, less rapidly than from sodium and water, so that the experiment is attended with no danger. The other product is *calcium hydroxide*, $Ca(OH)_2$, which is ordinary **slaked lime.**

$$Ca + 2\,H_2O \longrightarrow Ca(OH)_2 + H_2$$

Calcium is not found free in nature, but its compounds are so common that it ranks fifth among the elements in abundance. The earth's crust contains 3.5% of it, calculated as metal.

Barium and *strontium* resemble calcium closely. Barium and its compounds color the flame green, while the flame-color of strontium is crimson. The nitrates of both metals are used in fire-works.

412. Chemical Nature of Calcite.—When calcite is strongly heated, **lime**—which is *calcium oxide*, CaO—remains. If an iron tube is used for the heating, and the gas which escapes is passed into lime water, the liquid becomes cloudy, showing that carbon dioxide is evolved.

Quantitative knowledge can be obtained by intensely heating a weighed portion of powdered calcite in a crucible until it loses no more in weight. The result is that 100 parts lose 44 parts of carbon dioxide and leave 56 parts of lime. The molecular weight of lime, CaO, is 56. To find how many times CaO is to be taken in the formula we divide the 56 parts by weight of lime by the *molecular weight* of lime and find that there must be *one* CaO.

The 44 parts by weight of carbon dioxide, divided by its molecular weight ($CO_2 = 44$), shows that there is also *one* CO_2 in the formula of the mineral. The formula of calcite is therefore CaO, CO_2 or $CaCO_3$. The chemical name of calcite is *calcium carbonate.*

The reason that the calculation of the formula of calcite is so simple is that the molecular weight corresponding to $CaCO_3$ is just 100.

413. Calcium Carbonate.—*Marble* is often nearly pure crystallized calcium carbonate, but it is frequently beautifully veined and colored by small quantities of impurities. The specific gravity of marble is 2.7. *Limestone* is a compact form, not visibly crystalline, and not so pure. It is often colored blue, gray, or grayish black. Great quantities of it are used in the blast furnace, in making cement and lime, as a building-stone, and for road-making. *Chalk* is a soft limestone, composed of microscopic shells. Limestone composed of large shells cemented together is common in Florida. All limestones originated from animal remains, but some have been so changed that all traces of their origin are lost. Most shells are composed of calcium carbonate with organic matter. The *pearl* has the same composition.

414. Solubility of Calcium Carbonate.—Calcium carbonate is very slightly soluble in water (100 c.c. takes up 0.0013 gram), but water saturated with carbon dioxide dissolves about thirty times as much (100 c.c. takes up 0.0385 gram). Since all natural waters contain carbon dioxide, which they get from the decaying organic matter of the soil, they all dissolve calcium carbonate to some extent.

Water oozes through a bed of limestone until it comes to a water-tight layer, along which it runs, at the same time dissolving the limestone above. The result, in time, is a cavern, which may be many miles in length. The water begins to drip from the roof, and as soon as it appears there, some of its carbon dioxide escapes into the air. This causes some of the dissolved calcium carbonate to separate, so that a mass shaped like an icicle grows downward from the roof. This is called a **stalactite.** Where the drip strikes the floor, more carbon dioxide escapes and a mound of calcium carbonate called a **stalagmite** grows up. Often the two meet and form a column. Finally, the cavern may be filled up again by growths of this kind.

415. Lime.—We have seen that when calcium carbonate is heated it decomposes into lime and carbon dioxide:

$$CaCO_3 \rightleftarrows CaO + CO_2$$

Excepting the chemical changes of agriculture—which is really a branch of applied chemistry—the "burning" of lime is the oldest of chemical processes. It has been carried out, in connection with the making of mortar, for fifty centuries. It is a reversible change, limited at any fixed temperature by the concentration of the carbon dioxide.

If marble is heated in a sealed vessel to 550° it will decompose until the concentration of the carbon dioxide is great enough to produce a pressure of 27 m. m. of mercury. Then equilibrium sets in and there is no further change, so long as temperature and pressure remain the same.

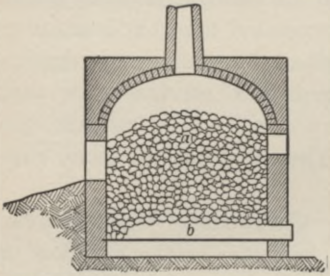


Fig. 94.—A simple limekiln.

If some of the carbon dioxide is now removed, say by an air pump, more marble will decompose, until the concentration of carbon dioxide which produces a pressure of 27 m. m. is restored. If the pump is kept in action, so that the pressure is not allowed to reach 27 m. m., the marble will all decompose and only lime will remain. On the contrary, if, at 550°, carbon dioxide is pumped into the vessel, so that its pressure is kept always above 27 m. m., all the lime will unite with carbon dioxide and pure calcium carbonate will result.

At any other temperature, the same thing holds good, but the limiting value of the pressure is different, being greater the higher the temperature. In the cold, this value is practically zero, so that lime, when exposed, unites with the carbon dioxide of the air and turns to calcium carbonate. This is one reason why lime does not "keep."

The practical result is that, in "burning" lime, the carbon dioxide must be removed as fast as it is formed; otherwise the change will stop as soon as the latter reaches the limiting concentration.

A simple limekiln is shown in Fig. 94. The fire is at *b*, below the limestone (*a*). The heat decomposes the limestone, and the constant current upward to the chimney carries off the carbon dioxide.

There are two bad defects about this arrangement. In the first place, it is wasteful of fuel, for much heat is carried off in the hot gases which rush up the chimney. All the heat in the finished lime is lost also, for it is simply chilled by opening the furnace and then taken out. Another defect is that every time a batch of lime is finished, the whole process must be stopped while the furnace is emptied and re-charged. Both these difficulties are overcome in the "ring furnace" which is widely used for "burning" lime, bricks and cement. It is really a group of furnaces (say fourteen) arranged in an oval around one chimney (Fig. 95). Each furnace communicates with a common smoke-canal which leads to the chimney, but the communicating pipe can be closed by a damper. The furnaces can also be thrown into communication with each other at will.

In the diagram, 13 and 14 are not in use. They are being emptied and refilled. 1, 2, 3, 4 and 5 contain finished lime. This is being cooled, but the heat is not wasted. Air enters at 1 and passes through the others to 6, which is the only furnace in which there is a fire. The air to support this combustion is *pre-heated.* by the waste heat of the finished lime in the first five furnaces.

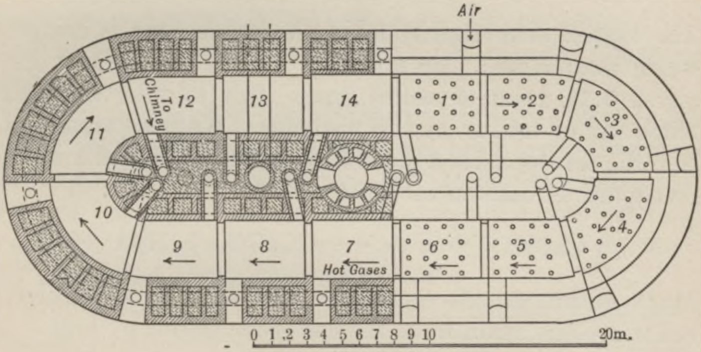


FIG. 95.—The ring furnace.

Furnace number 6 is not connected with the chimney. The hot gases are forced to pass through 7, 8, 9, 10, 11 and 12 and thence to the chimney. These compartments are filled with limestone, which becomes heated by the waste heat of the gases from 6.

After some hours, the fire is transferred to 7 and 13, which is now full of limestone, is connected to the chimney instead of 12; the finished and cooled lime is removed from 1, and the air enters at 2.

The furnace of Fig. 94 burns about 40 kilos of coal to produce 100 kilos of lime, but the furnace of Fig. 95 will produce the same result by burning only 20 kilos of coal.

Calcium oxide, CaO (*lime*), is a white solid which does not melt in the hottest flames, but, when strongly heated, gives out an intense light, called the "lime light." It can be melted and boiled at the temperature of the electric arc. It is used in making mortar, in the manufacture of soda, ammonia, bleaching powder and calcium carbide, in removing hair from hides and in the manufacture of glass.

416. Calcium Hydroxide.—When lime is sprinkled with water, it becomes hot and crumbles to a white powder of *calcium hydroxide*, "slaked lime."

$$CaO + H_2O \rightleftarrows Ca(OH)_2$$

The change is reversible, for if the slaked lime is heated, steam escapes and lime remains. 100 c.c. cold water dissolves 0.14 gram of slaked lime. This solution is called "lime water" and is used in medicine. We have employed it in the test for carbon dioxide, with which it forms a white precipitate of calcium carbonate:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O.$$

Much carbon dioxide causes the precipitate to re-dissolve, but it appears again when the gas is driven out by heat.

A small bit of calcium, thrown into water, liberates hydrogen and forms a clear solution of calcium hydroxide. If the air from the lungs, which contains over 4% of carbon dioxide, is bubbled through the liquid, it becomes milky from separated calcium carbonate; but if one blows through it for a long time, the latter dissolves and the liquid again becomes clear.

Mortar is a mixture of slaked lime and sand. At first it "sets," or hardens somewhat, by simple drying. Then a slow absorption of carbon dioxide from the air occurs, and the calcium carbonate binds the grains of sand into a stony mass. The sand tends to keep the mass porous and prevent shrinkage. In the middle of thick walls, mortar may remain soft for years.

Slaked lime stirred up with water is called "milk of lime." Whitewash is simply milk of lime. When painted on a wall, it absorbs carbon dioxide and forms a coating of calcium carbonate.

Calcium hydroxide is the *cheapest active base*, and is used, if it will answer the purpose, whenever a base is needed in chemical industry.

417. Hard Water.—Water containing dissolved calcium carbonate, or other calcium compounds, cannot be used for washing with soap, because it forms no lather, but produces, instead, a sticky film which is a calcium soap. The student should have no difficulty in explaining why water, whose hardness is due to calcium carbonate, can be softened by boiling, while, if the hardness is due to calcium sulphate, boiling has no effect.

Boiler scale is often due to dissolved calcium compounds, which are left as a hard coating when the water evaporates in the boiler. The student may also attempt to explain the curious fact that water, whose hardness is due to calcium carbonate held in solution by carbon dioxide, can be softened by adding the proper quantity of *lime.*

418. Strontium Hydroxide.—Strontium hydroxide, $Sr(OH)_2$, resembles slaked lime, but is much more soluble in water. It forms an insoluble compound with sugar, and is much used in beet-sugar works in separating sugar from liquids from which the sugar will not crystallize. The sugar can be again liberated by treating the compound with carbon dioxide.

419. Bleaching Powder.—In the manufacture of *bleaching powder* a layer of slaked lime 10 cm. deep is spread on the floor of a long, low chamber built of slabs of sandstone. Chlorine is passed in through a clay tube and is absorbed by the lime. The chamber is allowed to stand 12–24 hours, and then the finished bleaching powder is shovelled out.

It is a white powder which smells of chlorine. It is unstable and deteriorates on being preserved, more rapidly under the influence of light and warmth. There is still doubt as to the chemical nature of bleaching powder. It appears to contain a compound of the formula $CaOCl_2$, which liberates chlorine with acids:

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

Good bleaching powder yields 35% or more of its weight of chlorine when treated with acids, and all of its uses depend upon this fact. It is sometimes used as a disinfectant, but more often for bleaching cotton fabrics. The goods, sewed end to end into strips which are sometimes 50 kilometers long, are run by means of rolls into a dilute solution of bleaching powder and then into dilute sulphuric or hydrochloric acid, so that chlorine is set free in the fiber. Complex cleansing operations precede and follow the actual bleaching.

420. Barium Oxide, Barium Peroxide.—*Barium oxide,* BaO, is gray. When moistened it slakes to barium hydroxide, with such energy that it becomes red-hot. Heated to redness in a current of air, barium oxide absorbs oxygen and changes to *barium peroxide* BaO_2:

$$BaO + O \rightleftarrows BaO_2$$

The change is reversible and the direction in which it proceeds depends upon the concentration of the oxygen. Thus, if barium oxide is heated in an iron tube to 700° and air led over it, barium peroxide is produced. If now an air-pump is applied, the change proceeds from right to left (see equation above), all the oxygen which has been absorbed escapes, and barium oxide is formed again. Oxygen was formerly made in this way.

Barium peroxide, BaO_2, is a grayish-white powder, used in the manufacture of *hydrogen peroxide.*

421. Hydrogen Peroxide.—When barium *oxide* is treated with sulphuric acid, barium sulphate and water are formed:

$$BaO + H_2SO_4 \longrightarrow BaSO_4 + H_2O$$

When barium *peroxide* interacts with *concentrated* sulphuric acid, barium sulphate, water and *oxygen* are produced:

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O + O$$

Finally, when barium peroxide interacts with cold *dilute* sulphuric acid, no gas escapes. All of the oxygen unites with the hydrogen, forming *hydrogen peroxide,* H_2O_2, which dissolves, and can be separated from the barium sulphate by filtration:

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

Pure hydrogen peroxide is a thick liquid which smells like nitric acid. It has a faint blue color which is only perceptible in a thick layer. It is unstable, tending to separate into oxygen and water with explosion:

$$H_2O_2 \longrightarrow H_2O + O$$

Commercial hydrogen peroxide is a 3 % solution in water. It is used in bleaching wool, silk and feathers, and in surgery, for washing wounds. The bleaching power is due to the oxidation of the coloring matter by the loosely held oxygen. It is often called "20-volume solution" because it yields twenty times its volume of oxygen. This separation of the hydrogen peroxide into water and oxygen takes place very slowly but becomes very rapid in presence of certain catalysts, like platinum powder, or manganese dioxide.

Most oil paints contain compounds of *lead.* The darkening of paintings with age is partly due to the formation of lead sulphide by the action of sulphur compounds which escape into the air from the burning of coal and gas. Treatment with hydrogen peroxide oxidizes the dark lead sulphide into lead sulphate, which is white, and restores the original colors:

$$PbS + 4\,H_2O_2 \longrightarrow PbSO_4 + 4\,H_2O$$

Hydrogen peroxide usually acts as an oxidizing agent. But in some cases, it has the opposite effect. Thus when poured over silver oxide, oxygen escapes and water and silver remain:

$$H_2O_2 + Ag_2O \longrightarrow H_2O + 2\,Ag + O_2$$

The atomic theory suggests that the cause of this curious removal of oxygen from both substances is the tendency of the loosely held oxygen atom of the hydrogen peroxide to unite with the loosely held oxygen atom of the silver oxide, and form an oxygen molecule which, as we know, contains two atoms.

422. Ozone.—The *oxygen* which escapes when barium peroxide is treated with *concentrated* sulphuric acid has some properties which ordinary oxygen does not possess. It has a suffocating odor, slowly turns silver black, and gives a blue color to starch-potassium iodide paper, showing that iodine is liberated. This peculiar form of oxygen is called *ozone.*

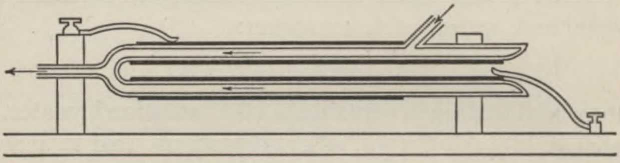


FIG. 96.—Tube for the conversion of ozone into oxygen.

Ozone is made by the action of electric waves on oxygen. The change is reversible, and when the concentration of the ozone has reached a certain point (5–10%, according to temperature and intensity of the electrical disturbance) no more ozone is produced. By cooling the mixture of ozone and oxygen with liquid air, pure ozone may be obtained as a deep blue black, explosive liquid which changes to a blue gas when withdrawn from the cooling agent.

One form of apparatus for the production of ozone (Fig. 96) consists of a double walled tube, coated inside and out with tin foil. Oxygen circulates between the walls and, by connecting the two layers of tin foil to the opposite poles of an induction coil, electric waves, like those made use of in wireless telegraphy, are made to pass through the oxygen.

The weight of a liter of ozone is 2.147 grams; hence 22.4 liters of it weigh 2.147 × 22.4 = 48 grams. Hence the formula of ozone is O_3. It is one and a half times as dense as ordinary oxygen.

Ozone contains more energy than oxygen:

$$3O_2 \longrightarrow 2O_3 - 68{,}000 \text{ Cal.}$$

Hence ozone is more active. It converts silver and mercury into oxides, bleaches dye-stuffs, and attacks organic matter. Rubber connections cannot be used in working with it. When ozone is passed through a heated tube, it is completely changed to oxygen. It is quite poisonous. The reputation it has attained for health-giving qualities is entirely undeserved. It is doubtful whether it is contained in the air. Ozone is employed in the purification of water. When air, charged with ozone, is allowed to bubble through the water, the micro-organisms in the water are destroyed.

423. **Carbonic Acid.**—Since calcium is bivalent, the formula of the acid corresponding to calcium carbonate, $CaCO_3$, would be H_2CO_3. It is called *carbonic acid.* Although the carbonates are numerous and familiar, the acid has never been obtained. The solution of carbon dioxide in water reddens litmus feebly and contains a little carbonic acid:

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

We might expect to obtain carbonic acid by adding sulphuric acid to a carbonate:

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2CO_3$$

It turns out, however, that the carbonic acid separates into water and carbon dioxide, so that the real result is:

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

Carbon dioxide, then, escapes, when a carbonate is treated with an active acid: and this serves as a test to distinguish carbonates from other substances. Most of the carbonates are "insoluble" in water. Sodium carbonate, ammonium carbonate, and potassium carbonate are freely soluble.

424. **Washing Soda.**—The *washing soda* of the household is a carbonate, as is shown by the brisk escape of carbon dioxide, when an acid is poured over it. The application of the flame test proves it to be a *sodium* compound. *Water* can be detected in the crystals by heating them in a dry test tube.

From the formula of carbonic acid, H_2CO_3, and the fact that sodium is univalent, we may predict that the formula of sodium carbonate will be Na_2CO_3. This is verified by quantitative work. By heating a weighed portion of washing soda crystals, and noting the loss in weight, it can be shown that they contain ten molecular weights of water, so that the formula is $Na_2CO_3\ 10\ H_2O$.

425. Sodium Carbonate.—The water of crystallization in washing soda makes up nearly two-thirds of its weight and plays no part in any of its uses. Hence it is prepared, shipped and sold on a large scale as Na_2CO_3, which is a white powder. To make the *crystals* and ship them would triple freight charges without yielding any advantage. The trade name of Na_2CO_3 is *soda*. In science, it is called sodium carbonate or, sometimes, *anhydrous* sodium carbonate (anhydrous meaning free from water).

426. Baking Soda.—Since carbonic acid contains two hydrogen atoms, it ought to be possible to replace only one by sodium, producing *sodium hydrogen carbonate*, $NaHCO_3$. This is the *baking soda* of the household. Following is a comparison of some facts concerning washing soda and baking soda:

Sodium Carbonate	*Sodium Hydrogen Carbonate*
White powder	White powder
Bitter nauseous taste	Taste saline, not unpleasant.
Poisonous	Not poisonous, largely used in medicine for indigestion, etc.
Melts undecomposed at red heat	Decomposed by gentle heat.
100 c.c. water dissolve 20 grams (18°).	100 c.c. water dissolve 8 grams (18°).
Used in soap-making, glass-making, etc.	Used in making baking powder, in cooking, and in medicine.

427. Applications.—Like other carbonates, baking soda liberates carbon dioxide with acids. The chemical fire extinguisher contains a bottle of sulphuric acid and a solution of baking soda, so arranged that the two chemicals are mixed at the time of use. The pressure of the carbon dioxide throws the stream, and the gas also plays a part in extinguishing the fire.

In cooking, baking soda is often used with sour milk. The *lactic acid* of the milk interacts with the baking soda, liberating carbon dioxide which is caught by the sticky gluten of the dough, giving the finished cake a light, porous structure. **Baking powder** contains, along with baking soda, some substance which will act upon it after the manner of an acid. "Cream of tartar" which is *potassium hydrogen tartrate*, $KHC_4H_4O_6$, is often used. Until the powder is wet, there is little action, for the contact between the two substances is not close enough, but when water is added they both dissolve and interact at once:

$$NaHCO_3 + KHC_4H_4O_6 \longrightarrow \underset{\text{"Rochelle salt"}}{NaKC_4H_4O_6} + H_2O + CO_2$$

Seidlitz powder is the same as baking powder, except that the materials are mixed only at the moment of use.

428. Solvay Process.—When *ammonium hydrogen carbonate* is added to saturated rock-salt solution, baking soda separates:

$$\underset{\text{ammonium hydrogen carbonate}}{NH_4\ HCO_3} + NaCl \rightleftarrows NaHCO_3 + NH_4Cl \qquad (1)$$

Ammonium hydrogen carbonate results when ammonia, water and carbon dioxide come together:

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3 \qquad (2)$$

Baking soda is easily changed by heat into sodium carbonate:

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \qquad (3)$$

These three chemical changes are the basis of the *Solvay process* by which nearly two million tons of sodium carbonate are made yearly.

A concentrated salt solution is saturated with ammonia gas in a closed iron kettle and then transferred to an iron tower 20 meters high containing perforated shelves. Here carbon dioxide, made by "burning" limestone, is passed in at the bottom under a pressure of three atmospheres. Equation (2) occurs first, then (1), and the baking soda separates upon the perforated shelves, which also serve the purpose of dividing the carbon dioxide into many little bubbles, to make it dissolve more easily. The baking soda is then heated in revolving iron cylinders to change it to sodium carbonate (3), the carbon dioxide being collected and used again.

The ammonium chloride solution, from the tower, is heated with lime, to obtain ammonia:

$$2\,NH_4Cl + CaO \longrightarrow CaCl_2 + H_2O + 2\,NH_3$$

The ammonia is used again. The calcium chloride solution contains the chlorine which entered the process as rock salt. Calcium chloride can be obtained from this solution by evaporation and some of it is recovered and sold, but it is difficult to market and is almost a waste product. Thus most of the chlorine is wasted. Another defect of the Solvay process is that the interaction in the tower is not complete. It is limited by the concentration of the interacting substances, so that only two-thirds of the salt enters the chemical change. The rest is wasted, going into the rivers with the calcium chloride. In spite of these bad features, the process is at present the cheapest way of making sodium carbonate, and it is worked on an enormous scale.

429. Potassium Carbonate.—*Potassium carbonate,* K_2CO_3, is a white powder similar to sodium carbonate. It is contained in wood-ashes, which were, for centuries, the sole source of it. Hence it is called "*potash,*" from which the name potassium has been derived. Nearly two thousand years ago the German tribes made soap by boiling potash with fat.

Crude *wool* is rich in potassium compounds, which pass into the wash water produced when wool is scoured. Much potassium carbonate is obtained by evaporating this water to dryness and heating the residue.

The *sugar beet* contains potassium compounds which dissolve with the sugar, when the beet is sliced and treated with water, and remain dissolved after the sugar has been extracted from the solution (p. 317). The liquid is then evaporated to dryness and heated to redness. This is an important source of potassium carbonate.

These three sources are examples of the intimate connection of potassium with animal and vegetable life. Potassium carbonate is also made at Stassfurt, from the potassium chloride which occurs there. It is a commercial product of importance, though not on the great scale of sodium carbonate. It is used in glass-making (hard glass) and for the preparation of other potassium compounds.

430. **White Lead.**—The important pigment *white lead* contains lead carbonate and lead hydroxide. Its composition is indicated by the formula, $Pb(OH)_2\ 2\ PbCO_3$. It is made by the joint action of acetic acid and carbon dioxide on lead. The acetic acid attacks the lead, forming lead acetate, which is then converted into white lead by the carbon dioxide.

In one process, finely divided lead, with acetic acid, is placed in a huge cask which rotates on a horizontal axis, and carbon dioxide is passed in.

In the *old Dutch process*, which yields a product unsurpassed in smoothness and covering power, a little acetic acid is placed in the bottom of an earthen pot, which is then filled with lead in folded thin sheets, or in cast gratings. Numbers of such pots are stood in spent tan-bark, which, in rotting, serves as a source of carbon dioxide. They are covered with planks upon which are placed a second layer of tan-bark, and another series of pots. This arrangement is repeated until the roof of the shed is reached. In about three months the lead is almost completely changed to white lead.

Related Topics

431. **Deliquescence.**—When potassium carbonate is exposed to air, it absorbs water, becomes damp, and finally forms a solution. The name *deliquescence* is applied to this behavior, which is also met with in many other substances.

The student will at once suspect that the *concentration* of the water vapor in the air must have a great influence upon deliquescence. That this is the case is shown by the fact that salt and sugar are both deliquescent at the seashore, on account of the increased concentration of the atmospheric water vapor. Hence, at the seashore, candy must be carefully protected from the air, and salt requires occasional baking to expel the moisture.

FIG. 97.—Apparatus for investigating deliquescence and efflorescence.

It is easy to make air *saturated* with water vapor. We need only to place a dish of water under a bell jar, Fig. 97. Its effect upon substances may be studied by placing them under the jar in watch-glasses. In this apparatus, *all solids which are soluble in water become deliquescent.*

432. **Efflorescence.**—Washing soda, when preserved, slowly loses water of crystallization and crumbles to a white powder. This is called *efflorescence.* Like deliquescence, it depends upon the concentration of the water vapor in contact with the substance. "Bluestone," $CuSO_4\ 5\ H_2O$, retains its water in ordinary air, but in very dry air it turns white and effloresces rapidly. Such air is easily made by placing a dish of sulphuric acid under a bell jar. Many crystals which are quite permanent in the open air will be found to effloresce in this apparatus, for the sulphuric acid takes up water vapor quickly, and keeps its concentration close to zero.

Most salts form several compounds with water. Thus $CuSO_4\ H_2O$, $CuSO_4 3H_2O$ and $CuSO_4 5H_2O$ are known. The last is always obtained when copper sulphate is crystallized from water solution in the usual way.

Some substances, when crystallized from alcohol solution, form crystals containing definite proportions of alcohol. This may be called *alcohol of crystallization.* Crystals containing ether, chloroform, etc., have also been obtained.

Definitions

Hard water. Water containing dissolved calcium or magnesium compounds, which prevent it from forming a lather with soap.

Boiler scale. A hard incrustation which forms inside boilers which are fed with water containing large quantities of calcium or magnesium compounds.

Deliquescence. The absorption of *water vapor* from the air, by a solid, forming a solution.

Efflorescence. The *loss* of *water of crystallization*, the crystals crumbling to a powder.

CHAPTER XXV

MATCHES, PHOSPHORUS, SUPER-PHOSPHATE FERTILIZERS, ARSENIC, ANTIMONY AND BISMUTH

433. **Distillation of Match-heads with Steam.**—A dozen heads, broken from ordinary (not safety) matches, are placed in the flask shown in Fig. 98. The flask, F_1, is half filled with water and the liquid distilled.

If this is done in a dark room, a ring of clear greenish light appears at *R*, where the steam condenses. After a time, little colorless spheres of a waxy solid collect under the water in F_2, which receives the drippings from the condenser. If the water is poured away, this solid begins to give off a white smoke, and is luminous in the dark.

This substance is the element **phosphorus**, which is part of the mixture of which the heads of matches are made. The symbol of phosphorus is P, the formula P_4, and the atomic weight 31.

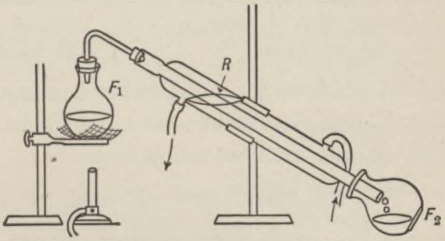


Fig. 98.—Extraction of phosphorus from match heads.

434. **Manufacture of Matches.**—In the manufacture of matches, the wooden splints are first dipped into melted paraffin to make them take fire more easily and then into a paste composed of:

Phosphorus, 4 to 7 per cent.
Lead dioxide (or some similar oxidizing agent), 50 per cent.
Warm water.
Dextrin, to bind the mass together (dextrin is the paste used for the backs of stamps. It is made by gently heating starch).
The head is then covered with lacquer to exclude air.

435. **Red Phosphorus.**—If the experiment of § 433 is tried with the heads of *safety matches*, no result is obtained,

for safety matches contain no phosphorus. But when we examine the box on which they are struck we find—cemented to it by dextrin—a purplish-red layer, which contains a *second modification* of phosphorus, called *red* phosphorus. Red phosphorus is very different from the *white phosphorus* contained in ordinary matches, as may be seen from the following comparison:

White Phosphorus	*Red Phosphorus*
Colorless	Purplish red
Specific gravity 1.8	Specific gravity 2.25
Takes fire at 34°	Takes fire at 240°
Oxidizes rapidly in air at ordinary temperatures	Oxidizes very slowly in air at ordinary temperatures
1 gram carbon disulphide dissolves nearly 10 grams	Insoluble in carbon disulphide
Luminous in the dark	Not luminous
Smells strongly of ozone	Odorless
Intensely poisonous	Not poisonous

Red phosphorus is made by heating white phosphorus to 260° for ten days in an iron kettle from which air is excluded. The change evolves much heat:

$$\text{P (white)} \longrightarrow \text{P (red)} + 27{,}000 \text{ cal.}$$

Hence the white form contains more *energy* than the red, and this is the cause of its greater activity.

The compounds made by combining the two forms with the same element are identical. In spite of the universal use of matches, the world's production of phosphorus is small (1000 tons per year).

436. **Safety Matches.**—The heads of safety matches are made of a mixture of sulphur or a combustible sulphide, like antimony sulphide, with an oxidizing agent like potassium chlorate, $KClO_3$. The box carries a layer of red phosphorus and powdered glass, cemented by dextrin. When the head is drawn over this coating, a little phosphorus is torn off, catches fire, and ignites the match. Safety matches can also be ignited by drawing them rapidly over glass, or some other smooth surface.

437. **Phosphorus Poisoning.**—White phosphorus is a violent poison and, on account of the ease with which it may be

obtained, is frequently employed by criminals. Treatment is difficult and complete recovery rare. The experiment of § 433 is frequently employed for the detection of white phosphorus in cases of suspected poisoning.

There is also a chronic phosphorus poisoning which attacks workmen in match-factories. The most characteristic symptom is a decay of the bones of the lower jaw. The use of white phosphorus, in making matches, is forbidden in many European countries. Burns, which may easily result from accidents in handling phosphorus, are quite dangerous and difficult to heal.

438. **Phosphorus Pentoxide.**—Either form of phosphorus burns readily, but with the white the combustion is more violent. A glance at the thermochemical equation for the change of white to red (p. 328) explains the reason. Red and white phosphorus yield the same product. It can be collected by placing a cold dry bottle over the burning substance. The glass becomes coated with a loose white powder, which has been shown to have the composition P_2O_5 and is called *phosphorus pentoxide.*

439. **Phosphoric Acid.**—When phosphorus pentoxide is thrown into water it dissolves, with a hissing sound, and the liquid becomes warm. On standing or boiling, *phosphoric acid,* H_3PO_4, is produced:

$$P_2O_5 + 3\,H_2O \longrightarrow 2\,H_3PO_4$$

Phosphoric acid, H_3PO_4, is a white solid which is very soluble in water. It is an active acid.

440. **The Calcium Salts of Phosphoric Acid.**—When *calcium* filings are thrown into a solution of phosphoric acid, there is immediate interaction, and, if sufficient calcium is taken, a white insoluble powder of *calcium phosphate* results. The student should recall the fact that calcium is bivalent:

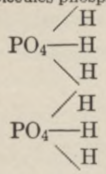
$$3\,Ca + 2\,H_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 3\,H_2$$

That this is not the only calcium salt of phosphoric acid becomes plain when a smaller quantity of calcium is used.

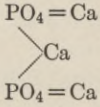
The metal dissolves, but the liquid remains *clear*. It contains *calcium hydrogen phosphate*, $Ca(H_2PO_4)_2$, which is freely soluble in water. A solution of this substance, made by a different method, is sold as a beverage under the name "acid phosphate."

The relation between these two substances and phosphoric acid will be made clear by the following formulas:

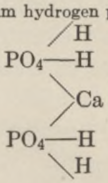
2 molecules phosphoric acid



Calcium phosphate



Calcium hydrogen phosphate



441. Minerals Containing Calcium Phosphate.—*Calcium phosphate*, $Ca_3(PO_4)_2$, is an abundant mineral in the United States and occurs in extensive beds in Canada, where it is mined. It is called *apatite*. Its crystals often have the hexagonal form shown in Fig. 99. They are about as hard as glass and are often sea-green. Crystals a foot or more in length have been found.

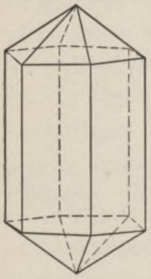


FIG. 99.—A crystal of apatite.

Great deposits of impure amorphous calcium phosphate (*phosphate rock*) occur in South Carolina, Tennessee and Florida, more than a million tons a year being obtained in the three states and used in the manufacture of *fertilizers*. Enormous deposits exist also in Idaho, Montana, Wyoming, and Utah.

White phosphorus is made by heating phosphate rock with coke and sand in the electric furnace shown in Fig. 100. The mixture is fed in at the hopper *H*, the graphite electrodes enter at *GG* and the slag is removed at *C*. Phosphorus vapor escapes through *P* and is condensed under water. The equation is:

$$Ca_3\,(PO_4)_2 + 3\,SiO_2 + 5\,C \longrightarrow 3\,Ca\,SiO_3 + 5\,CO + 2P$$

442. The Mineral Matter Required by Plants.—When a plant is burned, the organic matter is destroyed, and the ash which remains is derived from the mineral matter, which the plant, in its growth, took up from the soil. In order, therefore, to support plant-growth, the soil must contain the materials which the plant requires. Important among these necessary constituents are:

1 Magnesium
2 Calcium
3 Iron
4 Sulphates
5 Potassium
6 Nitrates
7 Phosphates

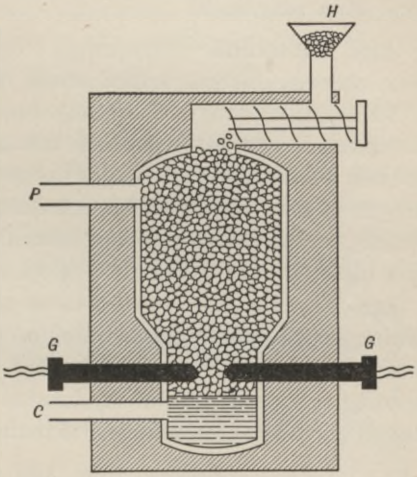


Fig. 100.—Manufacture of phosphorus.

The first four are present in such quantity in most soils that there is no fear of their exhaustion, even if one crop after another is grown and removed from the land. But the last three are not so plentiful and must be restored to the land to balance the constant drain by the crops; otherwise exhaustion and barrenness will result. We have already discussed potassium fertilization (p. 242) and nitrate fertilization (p. 306). The great source of phosphates for fertilization is the phosphate rock of the Southern and Western United States.

The rock can be powdered and put directly upon the fields, but it is very slow in its action, for calcium phosphate is "insoluble" in water and is only gradually taken up by the roots. Calcium hydrogen phosphate, $Ca(H_2PO_4)_2$, however, is soluble and gives a quick result. It is made on a large scale by treating the powdered phosphate rock with sulphuric acid in a closed iron vessel:

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\,CaSO_4.$$

As a rule, no attempt is made to separate the calcium sulphate from the product, for its effect is rather beneficial to the soil in most cases. The mixture of the two is sold as "superphosphate." It may be added that both apatite and phosphate rock usually contain calcium fluoride, CaF_2, mixed with the calcium phosphate.

The phosphorus compounds, which plants make from the phosphates of the soil, are found mainly in the fruit and seeds. Cereals are rich in them. From plants, phosphorus compounds find their way into the animal body. About 60% of the bones and teeth is calcium phosphate. Brain and nerve tissue contain large quantities of complex organic phosphorus compounds.

443. **Phosphine.**—*Phosphine,* PH_3, is a colorless, poisonous, combustible gas, which smells like rotten fish.

In a general way, with many exceptions, the phosphorus compounds are like those of *nitrogen.* Phosphine corresponds to ammonia, NH_3. This general relationship to nitrogen is also shown by the compounds of three other elements, *arsenic, antimony* and *bismuth.* Taken together, the five elements are called the *nitrogen group.*

444. **Arsenic** ($As = 75$).—*Arseno-pyrite,* FeSAs, is a silver-white, crystalline mineral, which occurs in many parts of the United States. When it is heated in a test tube, a black shining mirror of *arsenic* is formed in the cooler part of the tube, while iron sulphide remains in the bottom:

$$FeSAs \longrightarrow FeS + As$$

Arsenic is made by heating arseno-pyrite in a horizontal clay tube, into the mouth of which is fitted a rolled-up piece of sheet iron, to receive and condense the arsenic vapor. Arsenic is a brittle, crystalline solid. When fresh, it has a bright steel-gray luster, but it rapidly tarnishes and turns blackish. It is easily converted into vapor, and its vapor pressure reaches 760 m.m., and balances the pressure of the air, *before the melting-point is reached.* Hence it vaporizes *without melting.* When heated in vessels strong enough to withstand the pressure produced, it can be melted at about 500°.

About 0.5% of arsenic is added to the lead used in making **shot.** The melted alloy is then poured into a perforated iron basin at the top of the shot-tower. The drops fall 100–150 ft. into water. During the descent they become round, just as a rain drop does, because the natural shape of a liquid, left to itself, is the sphere. The arsenic lowers the melting point of the lead, making it more liquid and the shot more nearly spherical. It also makes the finished shot harder.

445. Arsenious Oxide.—When heated in the air, arsenic burns to a white smoke of *arsenious oxide,* As_4O_6. The oxide can also be obtained by heating arseno-pyrite in a current of air and leading the gases through chambers and canals in which the arsenious oxide deposits. It is obtained commercially as a by-product in the roasting of silver, copper, and nickel ores, many of which contain arsenic.

Arsenious oxide is a dense, white, crystalline powder, which vaporizes without melting and is somewhat soluble in water. It is a commercial product of considerable importance. It is added to melted glass to oxidize impurities and remove discoloration. Compounds made from it are widely used by the farmer and orchardist in destroying fungi and insect pests. It finds application in taxidermy and as a rat-poison.

Arsenious oxide is very poisonous (fatal dose, 0.2 gram or less) and, since it is easily obtained and has a feeble taste, it is frequently used by criminals. The poisons of the Borgias and the famous "Acqua Toffana," with which more than six hundred persons were slain, were prepared from it.

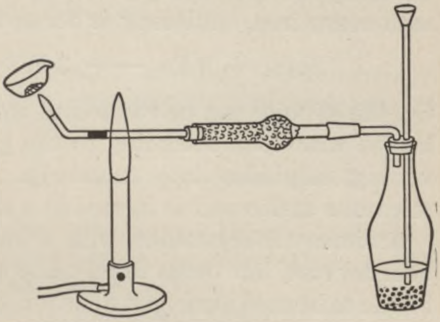


FIG. 101.—Marsh's test for arsenic.

446. Arsine.—*Arsine,* AsH_3, is a colorless gas with an offensive smell. It is poisonous in the extreme. When led through a tube heated to dull redness, it is decomposed and the arsenic condenses to a blackish-gray shining mirror. *Marsh's test* for arsenic is based upon this behavior.

When a solution of arsenious oxide is added to a liquid in which hydrogen is being generated, the nascent hydrogen combines with the arsenic and arsine escapes, mixed with hydrogen. For the lecture table, the hydrogen can be made in an ordinary gas bottle, from zinc and sulphuric acid and lighted. When a drop or two of a solution of arsenious oxide is poured in the funnel tube, the flame enlarges and becomes pale. If a porcelain dish is held in it, black-gray spots of arsenic are deposited. If the tube carrying the gas is heated, an arsenic mirror is obtained (Fig. 101). **This experiment is dangerous in unskilled hands.**

In practice, zinc is objectionable, for it usually contains arsenic and this might give rise to serious errors. The hydrogen is best made by the electrolysis of dilute sulphuric acid in a vessel divided into two compartments. Since hydrogen escapes at the cathode, the liquid to be tested is introduced into the cathode-chamber, and the hydrogen led away through a heated tube to see if an arsenic mirror results.

447. Antimony.—The chief ore of *antimony* ($Sb = 120$) is the blackish-gray, crystalline mineral *stibnite*, which is *antimony trisulphide*, Sb_2S_3. When it is melted in a crucible with scrap iron, antimony is formed:

$$Sb_2S_3 + 3\,Fe \longrightarrow 3\,FeS + 2\,Sb$$

Or, the stibnite can be roasted to antimony oxide and then heated with coal, according to the general method of converting sulphides into metal (p. 140). *Stibine*, SbH_3, resembles arsine and is formed in a similar way.

Antimony is crystalline, with a white metallic luster. It does not rust, but burns to an oxide when heated. It is too brittle to be used alone, but finds much application in hardening softer metals, especially lead and tin. Compounds of antimony are *poisonous*.

The bullets used in charging **shrapnel shells** are made of an alloy of 4 parts lead and 1 part antimony. Bullets of pure lead would be so soft that they would be mashed together by the explosion, and those which remained separate would be so changed in shape as not to carry far, when the shell burst. **Type metal** is an allov of about 75% lead, 15% antimony and 10% tin.

448. Bismuth.—*Bismuth* ($Bi = 208$) is found chiefly as metal. It is extracted by taking advantage of its low melting point (270°). The ore is heated in an inclined iron cylinder and the bismuth drains away from the other materials.

Bismuth is brittle. It can be distinguished from other metals by its pink luster, which is permanent, for bismuth does not rust. It burns to an oxide when heated.

Some alloys containing bismuth melt at a lower temperature than any of the metals of which they consist. Thus *Wood's fusible metal* contains:

4	parts	bismuth	(melting-point 270°)
2	parts	lead	(melting-point 327°)
1	part	tin	(melting-point 232°)
1	part	cadmium	(melting-point 320°)

The alloy melts at 60°. A spoon made of it would melt in a cup of hot coffee.

At bottom, the mechanism of fusible alloys is the same as the melting of a mixture of ice and salt below 0°. When two solids can melt *to form a solution*, their mixture will melt at a lower temperature than either alone.

Fusible alloys are used in automatic sprinklers. A pipe conveying water has a plug of fusible metal, which melts in case of fire and releases the water. Iron doors are held open by catches of fusible metal, which being melted by heat, allow the doors to close and shut off the burning portion of a building. Fuses in electric connections are made of fusible alloys.

449. Compounds of Bismuth.—Bismuth is trivalent. The hydroxide $Bi(OH)_3$ is a very inactive base and hence hydrolysis (p. 289) occurs when bismuth salts are dissolved in water:

$$\underset{\substack{\text{bismuth}\\\text{chloride}}}{\mathrm{BiCl_3}} + 3\,\mathrm{H_2O} \leftrightarrows \mathrm{Bi(OH)_3} + 3\,\mathrm{HCl} \tag{1}$$

Or, what is the same thing :

$$\underset{\substack{\text{bismuth}\\\text{ion}}}{\overset{+++}{\mathrm{Bi}}} + 3\,\overline{\mathrm{OH}} \rightleftarrows \mathrm{Bi(OH)_3} \tag{2}$$

Bismuth hydroxide is insoluble and forms a white precipitate. For this reason, bismuth salts cannot be dissolved clear in water alone. But if hydrochloric acid is added to the water in which bismuth chloride is dissolved, the reaction is forced, by the increase in the concentration of the acid, to proceed from right to left, and a clear solution results.

A compound which is at once an oxide and a nitrate of bismuth and which has the formula $BiONO_3$ is largely used in medicine. It is called bismuth *sub-nitrate*.

Related Topics

450. The Drying of Gases.—Phosphorus pentoxide absorbs water energetically, and one of the most effective methods known of drying a gas is to let it remain in contact with that substance.

No drying agent will *completely* absorb the water vapor from a gas. When the concentration of the water vapor has fallen to a certain limit, different for each substance, equilibrium results and no further drying takes place. The merit of phosphorus pentoxide is that the concentration of the water vapor in equilibrium with it is very small, much smaller than with other drying agents, like lime, calcium chloride or sulphuric acid. For the rapid drying of large volumes of gases in practical work, simple *cooling* is the cheapest method. The water vapor is condensed or frozen out of the gas. In the manufacture of iron, the blast of air for the blast furnace is frequently dried by passing it over coils of pipe, which are cooled by brine from an ice machine. The dry blast then goes to the blast stove and thence to the furnace. A decided saving in fuel results.

We have already met some examples of the fact that carefully dried gases are inactive chemically. A surprising instance is that, when oxygen has been dried by phosphorus pentoxide, white phosphorus can be melted (44°), or even boiled (290°) in it, without igniting.

CHAPTER XXVI

THE SILICATES AND BORATES

451. Water Glass.—The chief constituent of sand is *quartz*, SiO_2, often called *silica.* When clean white sand is melted with sodium carbonate, carbon dioxide escapes and *sodium silicate* remains:

$$Na_2CO_3 + SiO_2 \longrightarrow \underset{\substack{\text{sodium}\\\text{silicate}}}{Na_2SiO_3} + CO_2$$

Sodium silicate is a glassy mass, which is colorless when pure, but is usually colored green by iron silicate. Long boiling with water causes it to dissolve, and form a sirupy liquid. Hence it is called *water glass.* This solution is the form in which it is commonly sold. It is employed in fireproofing wood and cloth, as a cement, and as an addition to cheap soaps.

452. Glass.—Calcium carbonate interacts with silica at a high temperature:

$$CaCO_3 + SiO_2 \longrightarrow \underset{\substack{\text{calcium}\\\text{silicate}}}{CaSiO_3} + CO_2$$

When sodium carbonate and calcium carbonate are melted with silica, the product consists of sodium silicate and calcium silicate, which are united to form a substance which we may call *sodium calcium silicate.* This is ordinary *window glass.*

Glass is made by melting, in a large fire-clay pot, a mixture of (1) powdered quartz, or clean white sand, with (2) some form of calcium carbonate, such as limestone or chalk, and (3) sodium carbonate. *Sodium sulphate* is often used instead of sodium carbonate. It forms sodium silicate in a similar way and is cheaper.

The physical state of glass is just the same as that of the candy which is made by melting sugar and cooling it, without letting it crystallize. Such candy might almost be called "sugar glass." The liquid sugar, as it cools, becomes more and more viscous (stiff), until, when cold, it is so extremely viscous that we call it a solid. When this solid is heated, it softens more and more until we can call it a liquid, but there is no definite temperature at which it melts. When kept, such candy often turns to a mass of sugar crystals, which shows us that the glassy condition is unstable.

Glass, as we have seen (p. 8), behaves in exactly the same way when heated or cooled, and this softening makes glass-blowing possible. Like the sugar candy, it is in an unstable state. When melted glass is cooled too slowly, it sometimes crystallizes, which renders it opaque and makes it necessary to remelt it. In very old buildings, panes of glass are often found which have become crystalline and lost their transparency.

Lamp-chimneys, lenses and cut-glass objects are made of *flint glass.* This is *potassium lead* silicate, made by melting sand with potassium carbonate and lead oxide. It is denser than ordinary glass and refracts light more strongly. The "paste" which is used to imitate gems is flint glass rich in lead silicate, made by heating lead oxide and a little potassium carbonate with sand.

The student will remember, from his laboratory work, that many compounds of the metals dissolve in melted borax and color it. The same colors are produced in glass by the same means. The *green* of ordinary bottle glass is due to iron compounds. *Blue* glass is colored with cobalt compounds and manganese compounds yield an *amethyst* color. Imitations of colored gems, like the ruby, sapphire and emerald, are made by coloring "paste" in this way.

Plate glass, for mirrors and shop windows, is made by pouring melted glass on a cast iron table with a raised rim. The glowing glass is smoothed at once by a heated iron roll.

The more silica a glass contains, the higher the temperature required to soften it, and the better it resists the attack of chemicals. Ordinary glass contains about 70%, and *hard glass* more, up to 80%. More than 80% of silica makes glass so resistant to heat that it is difficult to work it on a large scale.

Pure quartz can be melted at a high temperature in a flame fed with oxygen, and worked into crucibles, thermometer tubes, beakers, etc. These articles are expensive. They will bear the full heat of the Bunsen flame without softening, and they can be heated red-hot and plunged into water without cracking.

453. **Clay.**—Just as a sulphate always consists of a metal united to sulphur and oxygen, so a *silicate* consists of a metal in union with silicon and oxygen, but, while the formulas of

the sulphates are simple, those of the silicates are very complicated.

Clay is *aluminium silicate*, $Al_2Si_2O_7$, white when pure, but often colored by iron compounds. Kneaded with water, it becomes plastic, and can be shaped at will into objects, which become stone-hard when dried and heated short of fusion. The manufacture of **bricks** and **terra cotta** is based upon this behavior. These materials are porous, for the clay shrinks in baking, and, since the external shape and size remain the same, the mass acquires a spongy structure.

Porcelain is made by baking a mixture of pure, white clay with powdered *felspar*. The temperature is pushed so high that the felspar melts and partly fills the pores which would be left in the clay.

Portland cement is made by heating a mixture of clay and limestone to a temperature at which the mass "sinters," but does not quite melt. It is then finely powdered. Cement consists of calcium aluminium silicate. When mixed with water, it sets to a stony mass, whose hardness and strength slowly increase for years. In actual use, it is always mixed with sand or broken stone. An excellent mixture is made by adding to the cement an equal weight of sand.

Cement is taking the place of natural stone for many purposes. More than five million tons of it are now made yearly in the United States, and the production is rapidly increasing.

454. **Some Natural Silicates.**—The silicates are very important rock-forming minerals. Limestone is the only common rock which is not composed of them. *Felspar*, which is aluminium potassium silicate, is the most abundant. It occurs in granite, and many other rocks, in crystals which often have a pinkish pearly luster. *Topaz*, *emerald* and *aquamarine* are examples of natural silicates used as gems. The *acids* corresponding to the various silicates have never been prepared.

Under the action of the weather, felspar slowly passes into clay, giving up its potassium, which, being extracted in soluble form, becomes available as plant-food. One of the great chemical problems of the future is the preparation of a potassium fertilizer from felspar, by making its potassium soluble in some cheap and rapid way. Such a process would at once make our country independent of the Stassfurt deposits, for the amount of potassium locked up in the felspar of our rocks is unlimited. A cubic yard of average granite contains about 250 lbs. of potassium; a cubic yard of felspar nearly 800 lbs.

455. **Borates: Borax.**—The familiar substance *borax* occurs as a mineral in Tibet, whence it was first obtained. That borax is a *sodium* compound is plain from its flame-color. That it contains water appears in the same experiment, for the borax froths and bubbles, when heated, because of the escaping water vapor. The acid of borax can be detected by powdering a little, moistening it with sulphuric acid, and adding alcohol. When ignited the alcohol burns with a green flame. This is the test for *boric acid.* Borax is *sodium tetra-borate.* Its formula is $Na_2B_4O_7 10H_2O$.

Boron, the characteristic element of borax, is a greenish-brown powder, insoluble in water. The addition of aluminium to melted steel before casting has been mentioned. Boron is sometimes added, for similar reasons, to copper, before casting. The boron removes any oxygen which may have combined with the metal, and improves the casting.

Borax is made from calcium borate, large deposits of which are found in Nevada, California and Bolivia. When the mineral is boiled with sodium carbonate solution, calcium carbonate and borax are formed.

Borax is used for cleaning metal surfaces for soldering. It dissolves and removes any oxide which may be on the metal and allows the solder to come into perfect contact. It is one constituent of the mixtures employed for glazing pottery and enamelled iron-ware. Some soaps contain it.

456. **Boric Acid.**—*Boric acid*, H_3BO_3, can be made by adding sulphuric acid to a solution of borax:

$$Na_2B_4O_7 + H_2SO_4 + 5\,H_2O \longrightarrow Na_2SO_4 + 4\,H_3BO_3$$

Boric acid forms white scaly crystals which feel greasy to the touch. 100 c.c. of water dissolves 4 grams at 18°. The solution is much used as an eye wash. Boric acid, when added to meats or other foods, prevents the development of the bacteria which produce decay. Hence it is employed as a preservative, but the addition of chemicals to food-products is a most objectionable practice.

Definitions

Silicate. A compound of a metal with silicon and oxygen.

Portland Cement. A calcium aluminium silicate which, when mixed with water, slowly hardens to a stony mass.

CHAPTER XXVII

CHROMIUM.—SOME IMPORTANT RARE ELEMENTS.—RADIO-CHEMISTRY

457. Chromium.—The chief native compound of *chromium* (Cr = 52) is the black mineral *chrome iron ore*, $FeCr_2O_4$, which comes mostly from Asiatic Turkey and from New Caledonia, a French penal settlement in the Pacific, east of Australia. Chrome iron ore is the raw material from which the chromium compounds of commerce are obtained.

Chromic oxide, Cr_2O_3, is called *chrome green*. It is a bright green powder used for painting on china. When it is mixed with aluminium filings and heated intensely at one point by means of a fuse prepared for the purpose, there is an energetic production of aluminium oxide and chromium:

$$Cr_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Cr$$

Chromium is made on a large scale by this method. It is a hard, bright, steel-gray metal, which melts at 2000°. It does not rust, but passes into chromic oxide when heated. It dissolves in hydrochloric acid, liberating hydrogen. Chromium has important applications in the making of special steels. Armor plate is often made of steel containing nickel and chromium. Tool-steels frequently contain chromium. "Invar" is steel containing 36% of nickel. It does not expand when heated, so that if the pendulum of a clock is made of invar the clock will run in exactly the same way in hot weather as in cold.

458. Potassium Dichromate. — *Potassium dichromate*, $K_2Cr_2O_7$, is made by heating chrome iron ore with potassium carbonate, K_2CO_3, and lime. The object of the lime is to keep the mass porous, which is necessary, because oxygen is absorbed in the chemical change.

Potassium dichromate forms orange-red crystals, soluble in about eight times their weight of water. It is employed in one type of electric battery, and in making chrome alum (p. 287) and chrome yellow. Its most important use is in tanning *chrome leather*, which is widely used, especially for shoes.

459. Potassium Chromate.—When a solution of potassium dichromate is mixed with potassium hydroxide, the orange color gives place to yellow and, on evaporation, yellow crystals of *potassium chromate*, K_2CrO_4, are deposited:

$$K_2Cr_2O_7 + 2\,KOH \longrightarrow 2\,K_2CrO_4 + H_2O$$

A solution of potassium chromate, mixed with an acid, turns orange and dichromate is formed:

$$2\,K_2CrO_4 + H_2SO_4 \longrightarrow K_2SO_4 + K_2Cr_2O_7 + H_2O$$

460. Chromium Trioxide.—When concentrated sulphuric acid is added to a cold, saturated solution of potassium dichromate, scarlet needles of *chromium trioxide*, CrO_3, separate:

$$K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2O + 2\,CrO_3$$

The liquid is poured off from the crystals which are dried upon a brick.

Chromium trioxide is a vigorous oxidizing agent. Warm alcohol dropped upon the crystals takes fire. It is often called *chromic acid*, but of course it is not an acid, since it contains no hydrogen. The true chromic acid which corresponds to K_2CrO_4 has the formula H_2CrO_4. It can be obtained in rose-red crystals, by cooling a water solution of chromium trioxide:

$$CrO_3 + H_2O \longrightarrow H_2CrO_4$$

It is very unstable, easily separating into chromium trioxide and water.

461. The Chromates.—The *chromates* of the heavy metals are yellow or red, poisonous and often insoluble in water. *Lead chromate*, $PbCrO_4$ (chrome yellow), is the most important. It is obtained, as a bright yellow powder, by mixing solutions of lead nitrate and potassium dichromate:

$$2Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O \longrightarrow 2PbCrO_4 + 2\,KNO_3 + 2\,HNO_3$$

It is largely used as a yellow pigment.

Sodium dichromate, $Na_2Cr_2O_7\ 2\,H_2O$, forms red crystals, much more soluble in water than potassium dichromate. It is cheaper than potassium dichromate and is displacing the latter in commerce. Sodium dichromate is made by heating chrome iron ore with sodium carbonate and lime.

462. **Tungsten.**—*Tungsten* is a metal which shows much chemical likeness to chromium. It is sold as a gray metallic powder, which can be melted only in the electric furnace. It is used for the filament of the tungsten lamp, which gives nearly three times as much light, for the same current, as the carbon incandescent lamp. Five per cent of tungsten, added to steel, makes it very hard, and the hardness is retained when the steel is heated and allowed to cool slowly, which is not the case with ordinary steel. The "self-hardening" tools, which can be used, without softening, at such speeds that they become red hot, are made of steel containing tungsten and chromium. Tungsten steels retain their magnetism remarkably well, and are much used in the construction of electrical measuring instruments.

463. **Thorium and Cerium—the Welsbach Mantle.**—*Thorium* and *cerium* are two rare elements which have as yet found no application as metals, but their oxides are important in connection with the *Welsbach mantle,* which contains 99% of *thorium oxide,* ThO_2, and 1% of *cerium oxide,* CeO_2. Departure from these proportions in either direction impairs the light, less cerium giving a feeble bluish-white light, and more, a dull yellow.

Monazite sand is the raw material of the mantle industry. It is found in reddish brown grains in the beds of streams in North Carolina, and in the beach-lands of the coast of Brazil. It is a phosphate of various rare elements, of which thorium and cerium are the important ones.

From it is prepared a solution of thorium nitrate containing a little cerium nitrate, and into this is dipped the mantle, which is woven of high-grade cotton or, sometimes, of ramie fiber or artificial silk. Heating over the Bunsen flame burns out the cotton and leaves a residue of thorium and cerium oxides, which retains the original gauzy texture. The mantle is then hardened by a blowpipe flame which has a high temperature. Dipping in collodion solution strengthens the mantle, so that it can be transported without breakage. When in use, the mantle is supported in a non-luminous Bunsen flame. All the light comes from the glowing mantle. Per cubic foot of gas consumed, the Welsbach mantle gives far more light than the naked flame.

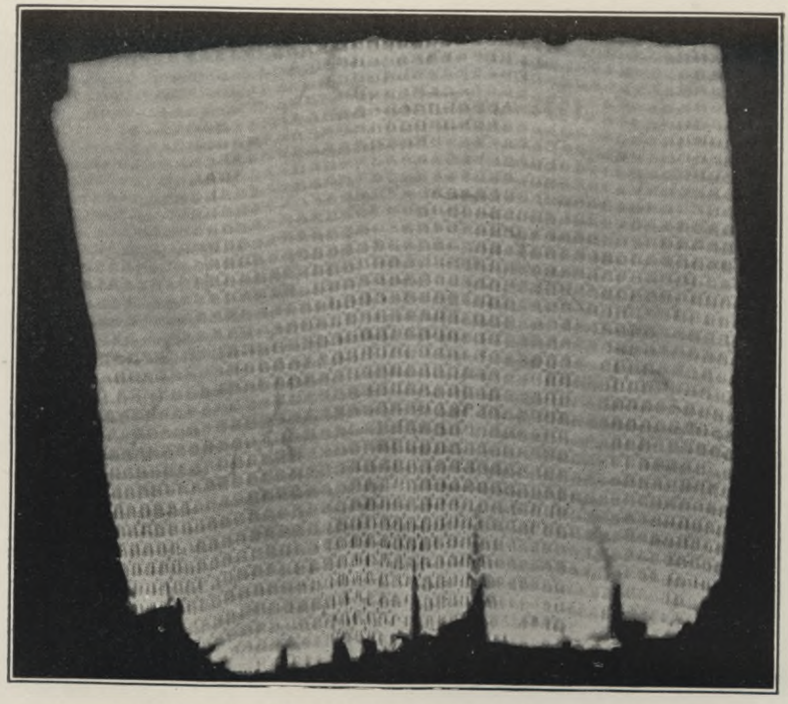


Fig. 102.—Action of the Welsbach mantle upon the photographic plate.

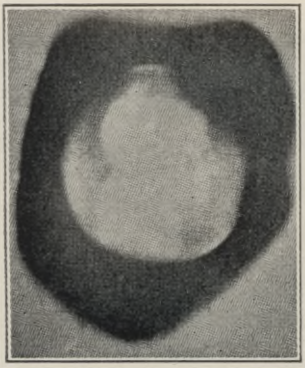


Fig. 103.—Photograph of a medal made by the rays from pitchblende.

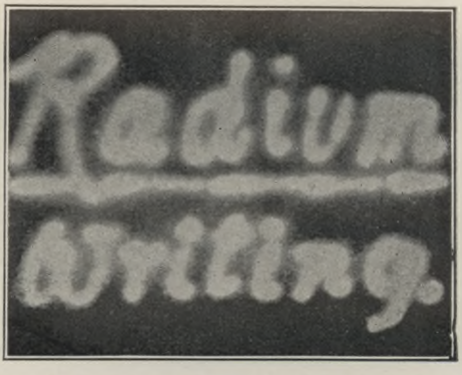


Fig. 104.—Effect of radium upon the photographic plate.

Related Topics

464. Radio-chemistry; an Experiment.—In a room lighted only by a dark-room lantern, a photographic plate is wrapped in black paper. Outside the paper, on the film side, a Welsbach mantle is flattened out by pressing it between the plate and a piece of pasteboard. The arrangement is enclosed in a light-tight box and left to itself two weeks. Then the plate is developed as usual. Fig. 102 shows the result.

The mantle has photographed itself upon the plate; therefore it must have given off rays which affect the plate in the same way as light. But these rays cannot *be* light, for light would have been stopped by the black paper. Further work shows that the radiation comes from the *thorium* of the mantle, for thorium, and all of its compounds, produce the effect, while cerium and its compounds are inactive.

465. Discovery of Radio-activity.—Our knowledge of radio-activity started in 1896 with an experiment similar to the above, made by Becquerel. He found that *uranium* compounds acted upon the plate, through black paper in a dark room.

Uranium is a white metal resembling chromium, but less common. Its compounds are mostly yellow, and are used in coloring glass. Uranium has the highest atomic weight of all the elements (U = 238). Its most important mineral is *pitch-blende*, U_3O_8, usually very impure.

Fig. 103 shows the result of one of Becquerel's experiments. There was an aluminium medal, with a head on it, between the uranium compound and the photographic plate.

If the radio-activity of pitch-blende was entirely due to the uranium, uranium itself would be more strongly radio-active than pitch-blende. *Madame Curie* found, however, that some specimens of pitch-blende which contained only 50% of uranium were four times as active as uranium itself. She drew the only possible conclusion; that pitch-blende must contain traces of some new element, much more radio-active than uranium, and she systematically worked up large quantities of pitch-blende to search for this substance. The result of these researches was the discovery of *radium*, which is more than a million times as radio-active as uranium or thorium. When a tube containing a strong radium preparation is simply drawn across a photographic plate, an impression is produced, which appears when the plate is developed (Fig. 104).

466. Radium.—*Radium* (Ra = 226) is a white metal belonging to the calcium group. It oxidizes easily in the air and is difficult to prepare. The actual work has been done with radium chloride, $RaCl_2$, and radium bromide, $RaBr_2$, which are white crystalline salts, soluble in water. The best pitchblende contains only one part of radium in five million, so that, to obtain an ounce of radium, more than 150 tons of the mineral would have to be worked up. The total quantity of radium thus far extracted, the world over, is probably less than an ounce.

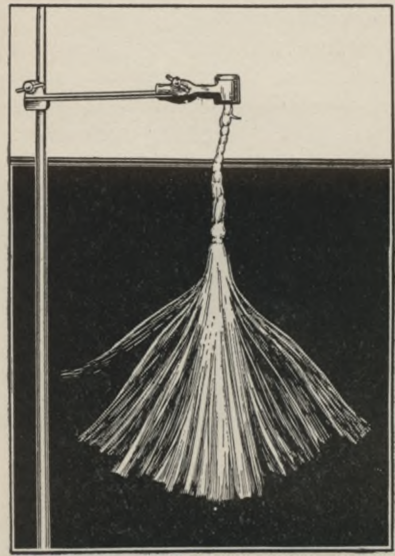


FIG. 105.—Electrified silk tassel.

467. Effects of the Radium Rays.—The radium rays turn white phosphorus to red, convert oxygen into ozone, cause diamonds, zinc sulphide and many other substances to shine in the dark, make paper turn brown and brittle, destroy the germinating power of seeds, and produce severe burns on the hands of chemists who use them. No matter how easy it may become to prepare radium, it will never be kept and stored in quantity, for, as Professor Curie said, if a man entered a room which contained a kilo of it, it would burn all the skin off his body and kill him. The action of radium upon the body has been applied, with some success, to the treatment of cancer and of lupus (tuberculosis of the skin).

Radium compounds are constantly a little warmer than their surroundings, that is, they give out *heat*. One gram of pure radium would give out more than 100 cal. per hour. Each hour it would give out enough heat to raise its own weight of water from the freezing- to the boiling-point.

Fig. 105 represents a silk tassel which has been charged with electricity by friction with a sheet of rubber. It retains its charge some time, for air is a non-conductor. But, when a radium compound is brought near, the charge is instantly lost (Fig. 106). *The radium rays make air a conductor.* Since methods of detecting conductivity in air are very perfect, this furnishes us with an inconceivably delicate test for radium or any radio-active element. Even the effect of a *single atom* of radium can be detected by its influence upon the conducting power of the air.

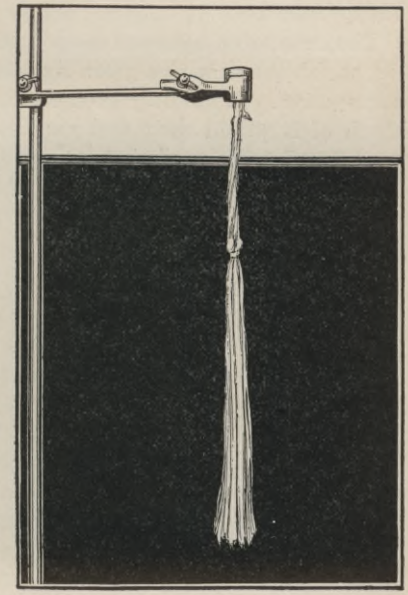
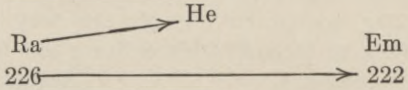


FIG. 106.—Silk tassel discharged by radium rays.

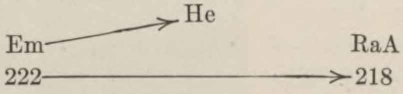
468. Nature of the Rays.—The puzzling thing about the matter is that all these effects of the rays mean a constant expenditure of *energy*. The idea of a substance radiating energy continuously, without taking in anything, is new in science. To explain the *source* of this energy is the problem.

The key to the solution was supplied, when it was shown that, unlike light, the radium rays are *material*. The most important rays, those which carry the greater part of the energy, and produce most effect in making the air conduct electricity, are atoms of *helium*, projected with the speed of 10,000 miles a second. The maximum speed attained by a rifle-bullet hardly exceeds one-half a mile a second.

469. The Radium Emanation.—The constant formation of helium from radium has been proved beyond doubt, and we must admit that the *radium atoms are unstable*, that they explode and shoot out helium atoms. What becomes of the radium atom after the helium atom has been pitched off? It can no longer be radium. Since Ra = 226 and He = 4 the atomic weight of the other product must be 226 − 4 = 222. It is a *dense gas*, called the radium *emanation*.

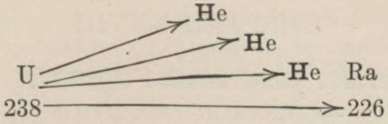


The emanation has been condensed by cold to a colorless liquid, which shines with a green light in the dark. It is intensely radio-active. It has only been obtained in very small quantity. Much of it would melt and vaporize any vessel in which it was placed. Its atoms shoot out helium atoms and, in so doing, it turns to a solid product of atomic weight 218, called *radium* A.



Radium A shoots out helium atoms and changes into other substances which we have not space to discuss. It is possible that the final product of the changes is *lead*. The total energy given out by a gram of radium in passing through all these changes is about a million times as great as can be obtained by the most energetic known *chemical* change of one gram of material. However, the change of radium takes place so slowly that 2500 years elapse before it is half complete, and there is no way to accelerate or retard it. In fact we have no control at all over radio-active changes.

470. Origin of Radium.—How is it that there is any radium left in the world? Why has not all of it long ago passed through its cycle of changes and disappeared? The only possible answer is that it must be continually produced afresh from some element of higher atomic weight. Since radium is always found in minerals containing uranium, there is strong reason to think that uranium is its parent. This belief has been confirmed by experiments, which show that uranium continually generates radium.



This change of uranium into radium takes place in several stages. We perceive, therefore, that the dream of the alchemists—the conversion of one element into another—has become a fact. We must, however, remember that we have no control over the process and can neither start it nor stop it.

CHAPTER XXVIII

SOME IMPORTANT COMPOUNDS CONTAINING CARBON. —COLLOIDAL SOLUTION

471. Nitroglycerine.—When alcohol is treated with nitric acid, *ethyl nitrate*, a colorless explosive liquid, is formed, the equation being similar to that for the neutralization of sodium hydroxide by nitric acid:

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

$$\underset{\text{alcohol}}{C_2H_5OH} + HNO_3 \longrightarrow \underset{\text{ethyl nitrate}}{C_2H_5NO_3} + H_2O$$

Compounds, like ethyl nitrate, in which the hydrogen of an acid is replaced by radicals composed of carbon and hydrogen are called **esters** (p. 239).

Glycerine, $C_3H_5(OH)_3$, is an alcohol containing three OH groups. Its behavior toward nitric acid is similar to that of a metal hydroxide containing three hydroxyl groups:

$$\underset{\substack{\text{aluminium}\\ \text{hydroxide}}}{Al(OH)_3} + 3\,HNO_3 \longrightarrow \underset{\substack{\text{aluminium}\\ \text{nitrate}}}{Al(NO_3)_3} + 3\,H_2O$$

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + 3\,HNO_3 \longrightarrow \underset{\text{nitroglycerine}}{C_3H_5(NO_3)_3} + 3\,H_2O$$

472. Manufacture and Properties.—*Nitroglycerine* is made by slowly adding one part by weight of purified glycerine to a mixture of 2 parts of nitric with 3 parts of sulphuric acid. The object of the latter is to concentrate the nitric acid by absorbing water from it. The mixture of acids is contained in a lead-lined vessel and is kept cold by water circulating in a coil of lead pipe, for, if the temperature goes above 25°, explosions occur. A large tank containing cold water is provided, into which the mixture can be run, in case the interaction becomes too vigorous.

The nitroglycerine floats on the surface of the acid mixture. It is removed and most carefully washed, with water and dilute sodium carbonate solution, to remove traces of acid, which make it liable to spontaneous explosion. 100 parts of glycerine yield 220 parts of nitroglycerine.

Nitroglycerine is a faint yellow, odorless oil with a burning sweet taste. It is poisonous and, in working with it, enough of its vapor is inhaled to produce dizziness and headache. In small doses it is used in medicine, as a powerful stimulant. It freezes at 12° and, when frozen, is unfit for use as an explosive. Many disastrous explosions have resulted from unskillful attempts to "thaw out" nitroglycerine mixtures.

473. **Explosion of Nitroglycerine.**—As a result of shock, friction, or sudden heating, nitroglycerine explodes with great violence. The chief explosion products are carbon dioxide, water and nitrogen-329,000 calories are liberated by the explosion of a molecular weight (227 grams).

As in the case of black gunpowder, the explosion is merely sudden oxidation, but in gunpowder the oxygen and the substance to be oxidized are in separate substances which are merely mixed—in nitroglycerine they are in the *same molecule.* Hence, with nitroglycerine, the explosion is more sudden and therefore more powerful. *Berthelot* showed, by direct measurement, that the explosion traveled along a tube filled with nitroglycerine, at the rate of 1300 meters a second.

Nitroglycerine is so easily exploded by shock that it cannot be transported. This difficulty was formerly overcome by soaking it up in porous earth, making a mixture called *dynamite,* which could be transported safely. This form of dynamite is now rarely used. Nitroglycerine is at present used chiefly in the form of "blasting gelatin" (p. 352).

It is clear that nitroglycerine is simply the *nitric acid ester* of glycerine. Its relation to glycerine is similar to that of sodium nitrate, $NaNO_3$, to sodium hydroxide NaOH.

474. **Nitrocellulose.**—*Cellulose,* $C_6H_{10}O_5$, interacts with a mixture of nitric and sulphuric acids in the same way as glycerine. The product is *nitrocellulose.*

The cellulose is used in the form of purified cotton fiber. It is allowed to remain in the acid mixture half an hour, then drained in a centrifugal machine and washed completely, first with cold and then with boiling water. The cotton is unchanged in appearance, but is harsher to the touch. Lighted with a match it burns with extraordinary energy, but without explosion. Friction between hard bodies, violent blows or sudden heating cause it to explode. Unlike nitroglycerine, nitrocellulose is not a single, definite chemical compound. We may roughly distinguish two varieties.

475. Guncotton.—In *guncotton* the interaction of the nitric acid with the cellulose has been pushed as far as possible, by using much sulphuric acid in the acid mixture (to absorb the water), and by allowing the cotton to remain in it till the action is complete. Guncotton contains upwards of 13% of nitrogen. Wet guncotton can be forced by hydraulic pressure into a hard mass which, while moist, can be bored and sawed like wood. This is employed for torpedoes (50–100 kilos for each) and for submarine mines.

The surest way of exploding guncotton, or any high explosive, is to *detonate* it. This means to explode, in contact with it, a small charge of some other substance, and set off the guncotton sympathetically. *Mercuric fulminate* is largely used for this purpose (p. 353). Guncotton is rarely used in practical blasting, since blasting gelatin (§ 478) is cheaper and more powerful.

476. Smokeless Powder.—A mixture of ether and alcohol does not dissolve guncotton, but converts it into a plastic mass which, when passed between rolls, comes out as a transparent sheet, not unlike horn. This, cut into leaflets 1 m.m. square or thereabouts, is the *smokeless powder* used by the United States, Germany, Russia, Japan, France and Austria. The English powder (Cordite) contains 65% guncotton, 30% nitroglycerine and 5% vaseline.

In addition to the absence of smoke, smokeless powder is much more powerful than black powder. Its introduction has doubled the effective range of the rifle, while the weight of the cartridge is only half that of the old black powder cartridge—a great advantage, since it allows the soldier to carry twice as many rounds of ammunition. A disadvantage is that the smokeless powder does not keep as well as the old black powder. When preserved, the smokeless powder undergoes slow changes which may lead to spontaneous explosion. Disastrous explosions have occurred on warships from this cause.

477. Collodion.—In making *collodion*, the action of the nitric acid on the cotton fiber is not pushed to completion. The product resembles guncotton in appearance but contains only 12 % of nitrogen and is not so explosive. It *dissolves* in a mixture of alcohol (1 volume) and ether (2 volumes) and the solution finds application in surgery and photography.

Celluloid is made by rolling collodion at a gentle heat with half its weight of camphor and a little alcohol. It is widely used for the backing of photographic films, and as a substitute for ivory, whalebone and amber.

478. Blasting Gelatin.—Nitroglycerine, warmed to 50°, dissolves nearly one-tenth of its weight of collodion. On cooling, the mixture solidifies to a transparent jelly called *blasting gelatin*. This is a more powerful explosive than either of its constituents; yet it can be transported safely, for it is not sensitive to shock or friction.

Pure blasting gelatin is too energetic for the use of miners and quarrymen. Instead of dislodging the rock in large masses, it converts much of it into powder. It is therefore mixed in practice with substances which moderate the intensity of the explosion. A common mixture consists of:

65% blasting gelatin
25% sodium nitrate
10% flour

Another contains:

50% blasting gelatin
45% ammonium nitrate
5% flour

In these mixtures the flour is burned, at the moment of the explosion, by the oxygen of the nitrate, but since this oxidation is much slower than the detonation of the blasting gelatin, the explosion is less violent and shattering. Such mixtures are called gelatin-dynamites. They have almost entirely taken the place of the old earth-dynamite, and of black powder.

479. Mercuric Fulminate.—*Mercuric fulminate*, $HgC_2N_2O_2$, is widely used as a **detonator** for high explosives. In making it, mercury is dissolved in an excess of moderately concentrated nitric acid at a gentle heat, and alcohol (10 c.c. for each gram of mercury) is added. There is a violent interaction, which is moderated by removing the flame. The mercuric fulminate separates in heavy white crystals, which are well washed with cold water.

The manufacture of mercuric fulminate is not dangerous in skilled hands, but the filling of the dry substance into cartridges and caps is a most perilous operation.

480. Esters of Acids Containing Carbon.—Although *acetic acid*, $C_2H_4O_2$ (p. 201), contains *four* hydrogen atoms, only *one* can be replaced in forming salts or esters. We may call attention to this fact by writing the formula $HC_2H_3O_2$.

When a mixture of alcohol and acetic acid is heated, *ethyl acetate* is formed:

$$C_2H_5OH + HC_2H_3O_2 \rightleftarrows \underset{\text{ethyl acetate}}{C_2H_5C_2H_3O_2} + H_2O$$

As the arrows indicate, the interaction is reversible: ethyl acetate interacts with the water formed, reproducing alcohol and acetic acid, so that equilibrium sets in when all four substances have reached a definite concentration. However, if sulphuric acid is added, to combine with the water, the backward change is prevented and the formation of the ethyl acetate goes on to completion.

Ethyl acetate is a colorless liquid, with a fragrant odor. The higher acids in the same series (p. 204) form esters in a similar way. Other alcohols can be used in place of ordinary alcohol so that a large number of esters can be made. They are chiefly liquids, having a pleasant, fruity odor. The artificial fruit essences, like essence of bananas, pears, pineapples, etc., are mixtures containing esters of this series.

The esters must not be confused with the *ethers*, which are the *oxides* of radicals like ethyl. Ordinary **ether** is *ethyl oxide* $(C_2H_5)_2O$. It is a colorless liquid which evaporates rapidly, when exposed to the air. It is made by gently heating alcohol with sulphuric acid. Ether is largely used as an anaesthetic.

481. The Fats.—The animal and vegetable *fats* are esters of the higher acids of the acetic acid series with *glycerine.* Thus butter is partly composed of the glycerine ester of butyric acid, $C_4H_8O_2$. Since only one hydrogen atom can be replaced, we write it $HC_4H_7O_2$.

The formation of this constituent of butter fat from glycerine and butyric acid could be written:

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{butyric acid}}{3\ HC_4H_7O_2} \longrightarrow \underset{\text{butyrine}}{C_3H_5(C_4H_7O_2)_3} + 3\ H_2O$$

The chemical name of this part of butter fat is *butyrine.*

The equation is not to be taken as meaning that butyrine is actually formed in this way from butyric acid and glycerine. It is intended merely to show the chemical nature of butyrine.

Palmitic acid, $C_{16}H_{32}O_2$ or $HC_{16}H_{31}O_2$, and *stearic* acid, $C_{18}H_{36}O_2$ or $HC_{18}H_{35}O_2$, both of which are white crystalline solids, belong to the acetic series (p. 204). Their glycerine esters, called *palmitine* and *stearine*, are important constituents of the fats:

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{palmitic acid}}{3\,HC_{16}H_{31}O_2} \longrightarrow \underset{\text{palmitine}}{C_3H_5(C_{16}H_{31}O_2)_3} + 3\,H_2O$$

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{stearic acid}}{3\,HC_{18}H_{35}O_2} \longrightarrow \underset{\text{stearine}}{C_3H_5(C_{18}H_{35}O_2)_3} + 3\,H_2O$$

It matters very little whether these fat-formulas are remembered or not, provided that the student gets a firm grasp of their meaning. He should think about them somewhat in this way:

(1) Nitroglycerine, $C_3H_5(NO_3)_3$, is constituted like $Al(NO_3)_3$. The difference is that, instead of a trivalent metal *atom* Al, it contains a trivalent *radical*, C_3H_5.

(2) Stearine, $C_3H_5(C_{18}H_{35}O_2)_3$, is like $C_3H_5(NO_3)_3$. The difference is that, instead of a univalent radical, NO_3, it contains the univalent stearic acid radical, $C_{18}H_{35}O_2$. Therefore the chain of ideas which links the fats to simple salts, like sodium nitrate, $NaNO_3$, is about as follows:

$$NaNO_3 \longrightarrow Al(NO_3)_3 \longrightarrow C_3H_5(NO_3)_3 \longrightarrow C_3H_5(C_{18}H_{35}O_2)_3$$

482. Soap.—When aluminium nitrate is treated with sodium hydroxide solution, aluminium hydroxide and sodium nitrate are produced:

$$Al(NO_3)_3 + 3\,NaOH \longrightarrow Al(OH)_3 + 3\,NaNO_3$$

Nitroglycerine interacts, in the same way, with sodium hydroxide: glycerine and sodium nitrate result:

$$C_3H_5(NO_3)_3 + 3\,NaOH \longrightarrow C_3H_5(OH)_3 + 3\,NaNO_3$$

When stearine is boiled with sodium hydroxide the chemical change is precisely similar: glycerine and *sodium stearate* are formed:

$$\underset{\text{stearine}}{C_3H_5(C_{18}H_{35}O_2)_3} + 3\,NaOH \longrightarrow C_3H_5(OH)_3 + \underset{\text{sodium stearate}}{3\,NaC_{18}H_{35}O_2}$$

Soap consists of *sodium stearate, sodium palmitate* and *sodium oleate* (which is the sodium salt of *oleic acid*, $C_{18}H_{34}O_2$).

In soap-making, a fat, like tallow, palm oil or olive oil, is placed in a large, open iron kettle, provided with a steam coil, and heated with a dilute solution of sodium hydroxide. When the formation of soap has begun, more concentrated sodium hydroxide solution is added, little by little. The soap boiler judges when his fat is completely changed to soap partly by the appearance, and partly by the fact that the bitter taste of sodium hydroxide remains, even after boiling the liquid, showing that the sodium hydroxide is no longer being used up in acting upon the fat.

When this point is reached, solid rock salt is added, which causes the contents of the kettle to separate into two layers. The lower is a water solution of glycerine, which, on account of its wide use in the explosive industry, is a valuable product. The upper layer is a semi-liquid mass of soap. It is run into iron forms, where it becomes solid, and is then cut into bars by means of a steel wire, stretched in a frame.

This product may still contain half its weight of water. In making the better grade of toilet-soaps, the crude soap is cut into shreds, dried, kneaded with perfume (and sometimes coloring matter), and pressed out in a long bar; which is cut into cakes, moulded and stamped. *Floating soaps* are made light by forcing air through them, while they are in a pasty condition.

Finished soap should not contain any sodium hydroxide, which is known as "free alkali" and is injurious to the skin. This means that the soap boiler must be careful not to use more sodium hydroxide than is needed to act upon the fat. The marked cleansing action of soap has not yet received a satisfactory explanation.

When soap is used with "hard water"—that is water containing calcium ions—no lather is formed, but calcium soaps—that is, calcium stearate, palmitate, etc.—are precipitated. Magnesium ions have a similar effect.

483. A Newer Method of Soap-making.—On account of its use in the explosive industry, the glycerine has now become as important as the soap, and it is difficult to prepare pure glycerine from the soap-liquor. For this reason another method of soap-making, by which pure glycerine is readily obtained, is coming into extensive use.

Let us take stearine, which is the chief constituent of beef and of mutton-fat, as an example. The fat is heated under pressure with superheated steam and a little lime. This converts it into glycerine and stearic acid:

$$\underset{\text{stearine}}{C_3H_5(C_{18}H_{35}O_2)_3} + 3\,H_2O \longrightarrow \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{stearic acid}}{3\,C_{18}H_{36}O_2}$$

The glycerine goes to the manufacturer of explosives. The stearic acid is sold to the soap boiler, who converts it into its sodium salt (soap) by boiling it with sodium *carbonate* solution:

$$2\,C_{18}H_{36}O_2 + Na_2CO_3 \longrightarrow \underset{\text{soap}}{2\,NaC_{18}H_{35}O_2} + CO_2 + H_2O$$

In addition to yielding pure glycerine, the method has the advantage that the soap boiler can use sodium carbonate, which is much cheaper than sodium hydroxide.

484. The Alkaloids.—The stimulating effects of tea and coffee are due to the presence of small quantities of a white crystalline bitter solid, called *caffeine*. Coffee, which has been deprived of its caffeine, is now an article of commerce and, while its flavor is the same as that of ordinary coffee, it has no effect upon the nervous system.

Caffeine is, in small doses, a brain stimulant, and, in large doses, a poison. It colors red litmus blue and interacts with acids, forming salts, and since, in these properties, it resembles the bases or alkalies, it is called an *alkaloid*.

There are many other alkaloids. They occur mainly in plants. Most of them are poisonous. Some of them, like morphine and cocaine, are invaluable medicines, but, when abused, become habit-forming drugs and produce the most

Alkaloid	*Formula*	*Source*	*Effect*
Atropine	$C_{17}H_{23}NO_3$	Nightshade	Dilates pupil. Used in eye-surgery.
Caffeine	$C_8H_{10}N_4O_2$	Tea and coffee	Brain stimulant.
Cocaine	$C_{17}H_{21}NO_4$	Coca-leaves	Local anaesthetic. Used in eye-surgery, etc.
Morphine	$C_{17}H_{19}NO_3$	Seed capsules of the opium poppy.	Narcotic
Nicotine	$C_{10}H_{14}N_2$	Tobacco	Narcotic
Quinine	$C_{20}H_{24}N_2O_2$	Bark of cinchona and other tropical trees	Used in treatment of fevers.
Strychnine	$C_{21}H_{22}N_2O_2$	Seeds of nux vomica	Powerful nerve and muscular stimulant.

destructive results. Most alkaloids are only slightly soluble in water and therefore their chlorides or sulphates are used in medicine.

The list on page 357 contains a few of the more important alkaloids. All those mentioned are white crystalline solids, except nicotine, which is a colorless, oily liquid. *The formulas should not be memorized.*

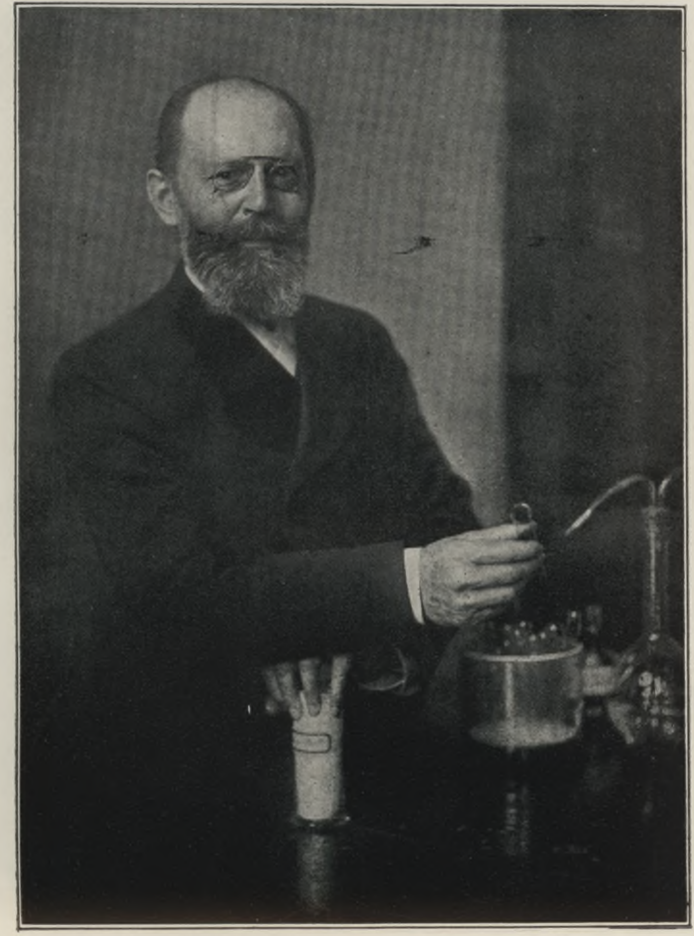
All alkaloids contain carbon, nitrogen and hydrogen. Most of them contain oxygen also.

485. The Albumins or Proteins.—White of egg consists chiefly of a compound which, when extracted in pure condition, is found to contain carbon, hydrogen, oxygen, nitrogen and sulphur (the student can remember these five elements by the syllable CHONS, made from their symbols). This compound is usually called *albumin* and is a type of a most important class of compounds called the *proteins*, which are always present in animal and plant substance.

All of the proteins contain the five elements just mentioned, and many of them also contain iron, phosphorus and other elements. They are a necessary constituent of human food; it is impossible to sustain life on a diet which does not contain them. Among foods rich in them are:

Meat	15% protein
Poultry	13–16% protein
Fish	12–16% protein
Eggs	13% protein
Cheese	27% protein
Beans or peas (undried)	7% protein
Chocolate	13% protein

Hardly any of the proteins can be obtained in crystals; hence it is difficult to purify them. They are very unstable; in fact it is their readiness to undergo chemical changes which fits them to serve as the raw material of the complex series of chemical changes which occur in digestion. For these reasons, the investigation of the nature of these bodies is a most difficult problem, and it is only recently that, owing



EMIL FISCHER

B. Germany, 1852

Synthetically prepared caffeine and many allied substances. Synthetically obtained glucose, fructose and many other sugars. Explained the chemical nature of the proteins and prepared artificially substances quite similar to them.

to the brilliant work of *Emil Fischer*, we have obtained a clear notion of their chemical structure.

486. Glue and Gelatin.—Certain portions of slaughtered cattle, like the hoofs, ears and tails, are unfit either for food or for tanning. Such refuse goes to the manufacturer of *glue* who boils it with water in steam-heated kettles. The skin-substance swells up, loses its structure and gradually dissolves. The clear solution, freed from undissolved matter, is evaporated until it contains 25% of protein, and is poured out upon a table covered with glass plates, which are cooled by water from below. Here it rapidly solidifies to a transparent plate, which is cut up and dried.

Gelatin is a pure glue, made from clean sheep-skin by the same method.

Related Topics

487. Colloids and Crystalloids.—Like almost all proteins, gelatin never forms crystals. *Thomas Graham* in 1861 was the first to point out that we must carefully distinguish crystalline from non-crystalline matter.

(1) Substances which formed crystals he called *crystalloids*. Such are salt, sugar, and almost all the substances studied in the preceding chapters.

(2) Substances which could not be obtained in crystals he called *colloids*, which means glue-like bodies. Starch, cellulose, almost all proteins, rubber and the gums are colloids. Our knowledge of the colloids is just in its beginning, but that they are important is plain from the great industries which are based upon them. A few of the industries which operate almost entirely with colloids are paper-making, photography, the various branches of the great textile industry, rubber manufacture, tanning, starch manufacture and agriculture. The bodies of animals and plants consist chiefly of colloids.

Fig. 107.—Dialyzer.

488. Colloidal Solution.—One peculiarity of colloids we have already noted. Unlike crystals, they have no melting-point, but soften gradually as they approach the liquid state. Another can be investigated by the apparatus of Fig. 107, which is due to Graham. It is called a *dialyzer* and is merely a shallow glass cylinder with a bladder, or other animal membrane, tied over one end. When a solution of table-salt is poured in this vessel—which is then placed with the bladder dipping into a little water in a dish—the salt passes through the membrane and divides itself between the outer and inner liquids.

Other crystalloids act like the salt—the membrane allows them to pass through it. But when a solution of gelatin, too weak to "set," is placed in the inner vessel, no gelatin penetrates the membrane and the water in the outer vessel remains free from it. Other colloids dissolved in water behave like gelatin—the membrane stops them completely.

FIG. 108.—Making a colloidal solution of gold.

We have seen that a solution of a crystalloid in water boils above 100° and freezes below 0°. But our solution of gelatin boils at 100° and freezes at 0°. *The boiling- and freezing-points of a colloidal solution are the same as those of the pure liquid.*

489. The Colloidal Solution of Gold.—Recent work shows that most "insoluble" substances can be obtained in *colloidal* solution if the proper conditions are supplied. Gold is an example. Two rods of pure gold are connected with a dynamo circuit of 220 volts and brought close together under the surface of distilled water (Fig. 108). The arc burns between the rods, with a clattering noise, and a purple color rises from them and fills the liquid.

The gold has been vaporized by the heat and the vapor is condensed so suddenly by the cold water that there is no chance for the molecules to collect into crystals: particles of gold containing only a few molecules are formed and these produce a colloidal solution in the water.

The purple liquid is clear, for the particles in it are too small to be detected even with the microscope. They can be examined, however, by the arrangement shown in Fig. 109, which is a simple form of the *ultra-microscope.*

In a darkened room a powerful beam of light is thrown by a mirror, S, against a lens, L, which focuses it, into the gold-solution contained in a little glass trough *b*. The liquid is examined with a good microscope. It is then seen to be filled with multitudes of red, yellow and green particles, all of which are in rapid, ceaseless, zig-zag motion. This motion does not stop, even if the preparation is preserved for years. It is the *heat motion of the molecules*, which becomes evident because the particles of gold are so extremely small. Except for the colors, the appearance is similar to that of a swarm of gnats, flying about in a sunbeam. The motion not only resembles in general character that required by the kinetic theory, but actual measurement shows that the speed of a particle and the average distance it moves in a straight line, before starting off in a new direction, are just about equal to the values obtained by calculation from the mathematics of the kinetic theory. Silver, platinum, copper and other metals can be obtained in colloidal solution by the same method.

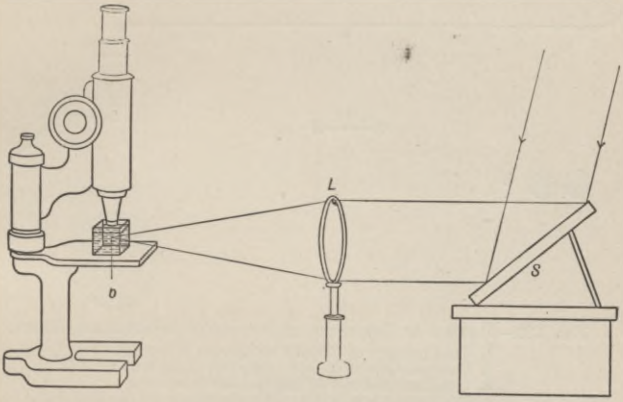


Fig. 109.—A simple ultra-microscope.

Fig. 110 shows the motion of gold particles of various sizes. Both particles and path are 3000 times the actual linear dimensions. The smaller the particle the more vigorous the motion, as we approach the dimensions of the single molecule. Still smaller are the molecules of gases, which move with about the speed of rifle-bullets, and beyond them, in the realm of the infinitely little, is the *electron*, a particle which weighs $\frac{1}{2000}$ as much as the hydrogen atom, and is shot out of some radioactive atoms with nearly the velocity of light. This appears to be the fundamental unit, of which the atoms of all the elements are built up.

An electric current is a swarm of electrons in *motion*. About a billion billion electrons pass each second through the carbon filament of an ordinary sixteen candle-power incandescent lamp. Thus, the difference between electricity and matter is that, in electricity, the electrons are independent of each other; in matter, the electrons are grouped, in an orderly way, to form the atoms of the elements.

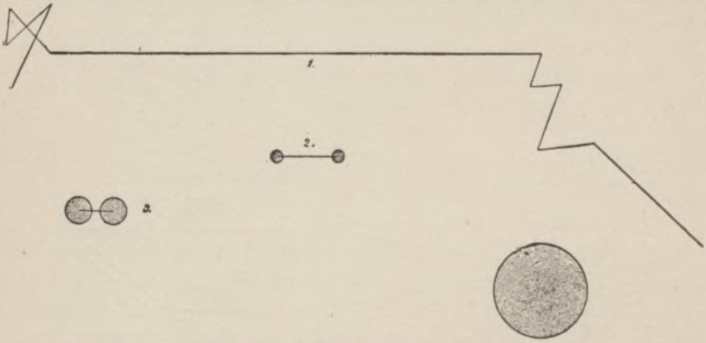


FIG. 110.—MOTION OF PARTICLES IN COLLOIDAL SOLUTIONS OF GOLD.
1. Gold particle of 0.00001 millimeter diameter.
2. Gold particle of 0.0005 millimeter diameter.
3. Gold particle of 0.001 millimeter diameter.
4. Gold particle of 0.004 millimeter diameter (motionless).
Magnified 1:3000

Definitions.

Ethers. The oxides of the hydrocarbon radicals. Ordinary ether is ethyl oxide $(C_2H_5)_2O$.

Soap. Sodium palmitate, sodium stearate, sodium oleate, or a mixture containing them.

Alkaloids. A class of plant products which are alkaline to indicators, form salts with acids and have a powerful action upon the body.

Colloids. Substances which, like glue, cannot be obtained in crystals.

Crystalloids. Substances which usually exist in crystallized conditions. Crystalloids can be obtained in colloidal condition, but they are then in an unstable state and tend to crystallize.

Colloidal Solution. The dispersion of a solid through a liquid, in particles so small that each can contain only a few molecules; an intermediate stage between suspension and solution. Both colloids and crystalloids can be obtained in colloidal solution.

Electrons. The minute particles which make up the atoms of the elements; the fundamental units of which matter and electricity consist.

CHAPTER XXIX

THE CLASSIFICATION OF THE ELEMENTS.—THE PERIODIC LAW

490. Nature of the Problem.—In our study of chemical *compounds*, we have found it necessary to *classify* them—that is, to divide them into groups in such a way that the members of each group exhibit a general similarity in properties. Examples of such groups are acids, bases, salts, esters, hydrocarbons and carbohydrates. We have now to inquire what progress has been made in classifying the *elements.*

We might begin by dividing the elements into *solids, liquids* and *gases.* More than sixty of the elements are solids. Only two, mercury and bromine, are liquids. Ten—chlorine, fluorine, hydrogen, nitrogen, oxygen and the five inert elements of the argon group—are gases.

Such a grouping would be of little service. The solids include such widely different elements as sodium, carbon and sulphur. Mercury and bromine show no chemical similarity. Among the gases, we find elements—fluorine, nitrogen and argon for instance—which exhibit such striking differences of chemical behavior that it is absurd to attempt to include them in the same group.

491. Metals and Non-metals.—A better classification of the elements is into *metals* and *non-metals.* Fifteen elements are *non-metals.* These are: arsenic, boron, bromine, carbon, chlorine, fluorine, hydrogen, iodine, nitrogen, oxygen, phosphorus, selenium, silicon, sulphur and tellurium.

The inert elements of the *argon* group are non-metals, so far as their physical properties are concerned. Since they have no chemical properties, they form a class by themselves. They are: argon, helium, krypton, neon and xenon. All of the remaining elements, sixty or more, are *metals.*

492. Physical Properties of Metals and Non-metals.— When polished, the metals have a peculiar luster called the *metallic* luster. This is due to the fact that they are very opaque and hence, when polished, reflect regularly most of the light which falls upon them.

The metals are *tenacious*. An iron wire, suspended vertically, would reach a length of two miles and a half, before it would break of its own weight. Steel is much more tenacious than iron. A steel rod, 1 square centimeter in cross section, requires a force amounting to the weight of 8000 kilograms to pull it asunder. The other metals are inferior to iron and steel in tenacity, but those which are in common use, like copper, zinc and tin, are far more tenacious than the non-metals.

The metals are more or less *ductile:* that is, they can be drawn into wire. One gram of gold can be drawn into a wire three thousand meters in length.

The metals are more or less *malleable:* that is, they can be beaten out under the hammer. Gold, which is by far the most ductile of the metals, is also the most malleable. It can be beaten into leaf less than 0.00001 centimeter in thickness.

The solid *non-metals* are *brittle.* When struck with a hammer they are crushed to pieces. They cannot be beaten into foil nor drawn into wire. The metals are good conductors of heat and of the electric current, silver standing first in both respects. The non-metals are non-conductors or very poor conductors, both of heat and of the current.

Several *exceptions* to the above statements must be noted. *Antimony,* which is commonly regarded as a metal, is very brittle. Sodium, potassium and some other metals have little tenacity. *Iodine, graphite* and *silicon* resemble the metals in luster. *Graphite* is a fairly good conductor of the current and, on this account, is widely used for electrodes in the electro-chemical industries.

493. Chemical Properties of Metals and Non-metals.—The hydroxides of the metals are *bases*. Sodium hydroxide and potassium hydroxide are familiar examples. Many of the metallic hydroxides are insoluble in water—those of nickel, copper and iron for instance—and these cannot, of course, affect the color of red litmus, but they can still be considered as bases in the sense that they interact readily with acids, forming salts. **The metals, therefore, are base-forming elements.**

On the contrary, the non-metals show a tendency to enter into the composition of *acids*. Hydrochloric, nitric and sulphuric acids are striking instances of acids composed of non-metallic elements. Acids containing metals are known, but they are unstable and unimportant. **The non-metals, therefore, are acid-forming elements.**

Another interesting distinction is in the *hydrogen* compound of the two classes. The hydrogen compounds of the non-metals are rather stable and are mainly *gases*. Water, which is a liquid easily converted into a gas, is the chief exception.

Very few of the *metals* combine with hydrogen. The metal-hydrogen compounds which have been obtained are *solids* and are very unstable, being easily decomposed, at a slightly elevated temperature, into metal and hydrogen.

The most striking property of the atoms of the metals is their tendency to form *positive ions* in water solutions. When a salt of a metal is dissolved and ionized, the metal atom forms the positive ion and the rest of the molecule the negative. For example see table on opposite page.

Positive ions composed of single atoms of non-metals, other than hydrogen, are unknown. It follows from this that *salts* in which the hydrogen of acids is replaced by single atoms of non-metals are impossible. Such an impossible compound would be, for example, chlorine nitrate, $ClNO_3$. The chlorine atom cannot take up a positive charge, and the compound cannot exist.

All this may be summed up briefly in the statement that hydrogen and the metals are *electro-positive,* while the non-metals are *electro-negative.* An important practical result is that the metals are always deposited at the *negative pole* during electrolysis.

494. Classification of the Metals.—During the middle ages the metals were divided into the *"base metals,"* which lost their luster and were converted into oxides when heated, and the *"noble metals,"* which were not changed into oxides when heated and were said to "stand the fire test." Copper is an example of the first class and gold of the second.

Substance	*Molecule*	*Positive Ions*	*Negative Ions*
Sodium chloride	$NaCl$	$\overset{+}{Na}$	$\overset{-}{Cl}$
Sodium nitrate	$NaNO_3$	$\overset{+}{Na}$	$N\overset{-}{O}_3$
Sodium sulphate	Na_2SO_4	$2\,\overset{+}{Na}$	$\overset{--}{SO_4}$
Sodium acetate	$NaC_2H_3O_2$	$\overset{+}{Na}$	$C_2\overset{-}{H}_3O_2$

It is clear that the difference is simply one of chemical activity. Gold is an *inert* element. It has little tendency to combine with other elements, and its compounds, when formed, are easily decomposed. Hence, when gold is heated in the air, no combination with oxygen occurs. On the contrary, gold oxide, Au_2O_3, is easily decomposed by heat. Copper is far more active than gold, so that, when heated, it combines with oxygen, and the compound, once formed, is not easily decomposed by heat.

The noble or "precious" metals, therefore, are simply those whose chemical activity, compared with that of the other metals, is slight. Since metals of this class occur only in small quantities in the earth's crust, they are costly.

495. Light and Heavy Metals.—A rough but serviceable classification is into *light* and *heavy* metals. The *light* metals include those, like sodium, potassium and calcium, whose specific gravity is less than 5. The *heavy* metals are those, like copper, lead, tin and iron, whose specific gravity is greater than 5. This latter class includes almost all the metals in common use.

The *light metals* are *active.* They burn energetically when heated. Many of them are rapidly converted by water into their hydroxides, hydrogen escaping. Their tenacity is very much less than that of the heavy metals. These properties unfit them for constructive work. The *heavy metals* combine with oxygen and interact with water much less rapidly than the light metals. They are more ductile, malleable and tenacious. Some of them are constructive materials of enormous importance.

Owing to their chemical activity, the light metals are somewhat difficult to separate from their compounds. Their preparation in the free state could not be effected until the methods of our science had developed sufficiently to accomplish the task. They were obtained in fairly pure condition during the 19th century. Many of the heavy metals, especially the more abundant ones, were known to the ancients.

Aluminium occupies an exceptional position. Its specific gravity (2.6) places it with the light metals. In agreement with this stands the fact that it is difficult to obtain from its compounds. But, when once separated, aluminium is little acted on by air and water, and can be applied to many purposes for which the other light metals are entirely unsuitable. This peculiar behavior is due to the fact that an invisible film of aluminium oxide forms on the surface. This film acts like a varnish, and protects the metal beneath.

496. Natural Families of Elements.—We have already discussed the chlorine group, often called the *halogens,* as an example of a natural family of elements. Another good example of a natural family is the *sodium group,* consisting of the following elements:

Name	*Symbol*	*Atomic Weight*	*Spec. Gravity*	*Melting-Point*
Lithium	Li	7	0.6	186°
Sodium	Na	23	0.95	96°
Potassium	K	39	0.86	63°
Rubidium	Rb	85	1.5	38°
Caesium	Cs	133	1.9	27°

Like sodium, the other members of the group are nearly silver-white metals, soft enough to be cut with a knife. A glance at the right-hand column shows that, as the atomic weights rise from Li = 7 to Cs = 133, the melting-points fall. Caesium is a liquid on a warm summer day. In specific gravity, a gradual increase can be traced from lithium to caesium, though the regularity is broken by potassium, which is a trifle less dense than sodium.

The chemical activity increases regularly from lithium to caesium. One instance of this is the interaction of the five metals with water. They all liberate hydrogen rapidly, forming their hydroxides, thus:

$$\mathrm{Li} + \mathrm{H_2O} \longrightarrow \mathrm{LiOH} + \mathrm{H}$$

In the case of lithium, the temperature does not rise high enough either to melt the metal or to ignite the hydrogen. Sodium melts, but the hydrogen does not usually catch fire. With potassium, ignition of the hydrogen always occurs. Rubidium, and especially caesium, explode violently with water.

Under the *halogens* (p. 258) we discussed a similar case of gradual variation in chemical activity with varying atomic weights. Such instances force upon us the question as to whether the properties of an element do not *depend* upon its atomic weight in somewhat the same way as the area of a circle depends upon its radius. In mathematical language, the question is whether the properties of an element are *functions* of its atomic weight.

497. The Electron.—The subject may be looked at from another point of view. The facts of radio-activity, and other facts whose detailed discussion belongs to Physics, indicate clearly that the actual material of which the atoms consist is the same in all the elements. The *electron* is a particle which seems to weigh about $\frac{1}{2000}$ as much as a hydrogen atom. The atoms of the elements are groups of electrons. All of the atoms of the same element contain the same number of electrons, but the numbers in the atoms of different elements are different and are proportional to the atomic weights. For instance, it must take about twice as many electrons to make an atom of nitrogen (N = 14) as to make an atom of lithium (Li = 7). Since the different properties of the elements can only be due to the different number and arrangement of the electrons, we are led to expect a very real connection between the properties of an element and its atomic weight.

498. The Periodic Law.—The way to investigate this connection is to arrange the elements in the order of increasing atomic weights and ascertain how their properties vary as the atomic weights increase. Omitting hydrogen, here are the first sixteen elements:

0	1	2	3	4	5	6	7
Helium	Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine
He = 4	Li = 7	Be = 9	B = 11	C = 12	N = 14	O = 16	F = 19
Neon	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine
Ne = 20	Na = 23	Mg = 24	Al = 27	Si = 28.5	P = 31	S = 32	Cl = 35.5

Helium is one of the chemically inactive gases of the argon group, lithium is a metal very similar to sodium, fluorine is a gas which resembles chlorine very closely and is the most active of all the non-metals. The elements between the two are intermediate in character: any element is less metallic than the element to the left of it. Thus in passing from lithium to the right there is a gradual loss of metallic properties, which finally, when we arrive at fluorine, is complete.

Now the next element in order is neon (Ne = 20), one of the inert gases of the argon group. There is no gradual transition from fluorine to neon. We pass at once from the most active non-metal to a completely inactive element. After neon comes sodium (Na = 23), one of the most positive of the metals. There can be no doubt that sodium belongs in the same group as lithium, for the two resemble each other in a remarkable way. This is true also of the elements which follow sodium in the second line; each is like the one above it in the first line. Magnesium is similar to beryllium, aluminium to boron, and so on. This similarity is greater at the ends than in the middle of the table. Sodium is more similar to lithium, and chlorine to fluorine, than aluminium is to boron, or silicon to carbon. Yet the similarity between these middle elements is great enough to show that they belong together.

499. The "Law of Octaves."—Thus these two sets of eight elements each exhibit a relationship like that of two octaves in music:

1st octave	C	D	E	F	G	A	B	C
2d octave	c	d	e	f	g	a	b	c

In fact, when this remarkable arrangement of the elements was first brought forward, it was called the "law of octaves" for that reason. The properties of the elements change with increasing atomic weight, and the change is a *periodic one*—that is, similar elements occur again and again as the atomic weight increases, very much as the hours repeat themselves in different days, or the seasons in different years.

This periodic change in properties, with increasing atomic weight, is the root-idea of the periodic law, and, if all the elements behaved like the first sixteen, the whole matter would be very simple. We should arrange the elements, in the order of increasing atomic weights, in horizontal lines, each containing eight elements, and those elements falling in the same vertical line would belong together and would show similarity in properties. We shall see at once that the real state of things is more complicated than this.

500. Long and Short Periods.—The set of elements from helium to fluorine we call the *first short period,* and that from neon to chlorine the *second short period.* The next eighteen elements in the order of increasing atomic weights are the following.

This set begins, as we should expect it to, with an inactive gas. Then follows a metal (potassium) whose similarity to sodium and lithium is very great. Farther along in the first line, we discover that we have here a different arrangement from that of the short periods. Chromium is not very similar to oxygen and sulphur, in whose vertical group it falls, for it is much more metallic in character; while the similarity between manganese, on the one hand, and fluorine and chlorine on the other, is remote, manganese being, in most of its chemical conduct, a metal. Yet, though in both cases the elements differ from the corresponding ones of the short periods, there are still some striking points of similarity which justify us in classing chromium with oxygen and sulphur, and manganese with fluorine and chlorine. One important difference between this arrangement and that of the short periods is, then, that at the element numbered 7—manganese in this case—the metallic properties have partially but by no means completely disappeared. Further, the next metal, iron, is by no means an inert gas like argon, as it should be if it stood at the beginning of a new short period. The three elements of the column numbered 8—iron, cobalt, and nickel—resemble each other strongly. Copper is not nearly as positive a metal as potassium. In the last seven elements, from copper to bromine (Br = 80), there is a gradual and complete disappearance of the metallic characteristics. Bromine is an unmistakable non-metal, and belongs in the same group as fluorine and chlorine.

0	1	2	3	4	5	6	7	8		
Argon Ar = 40	Potassium K = 39	Calcium Ca = 40	Scandium Sc = 44	Titanium Ti = 49	Vanadium V = 51	Chromium Cr = 52	Manganese Mn = 55	Iron Fe = 56	Cobalt Co = 59	Nickel Ni = 58.7
	Copper Cu = 63.5	Zinc Zn = 65.5	Gallium Ga = 70	Germanium Ge = 72	Arsenic As = 75	Selenium Se = 79	Bromine Br = 89			

This set of eighteen elements is called the *first long period*, and the general plan on which a long period is built is this: First stands one of the inert gases of the argon group, and second one of the active metals of the sodium group. In the following six elements the metallic qualities diminish, but do not completely disappear, so that the element numbered 7, manganese, for instance, shows mixed metallic and non-metallic characters. The position of the three following elements is peculiar. Their atomic weights lie near together (compare the atomic weights of iron, cobalt, and nickel), and they resemble each other strongly. Finally, through the remaining seven elements the metallic properties gradually and completely vanish, so that the last member of the long period is, in all respects, a non-metal.

501. Grouping of the Elements According to the Periodic Law.—The complete arrangement of the elements according to the periodic law is given in the table on page 374. The vertical columns are called **groups**, and the student will be prepared to find that elements in the same group resemble each other. It is convenient to divide each group into two **sub-groups,** and the resemblance between members of the same sub-group is especially close. Thus, in group 1, the members of the *sodium group*, lithium, sodium, potassium, rubidium, and caesium, resemble each other far more than they resemble the elements of the *copper group*, copper, silver, and gold. The elements of group O are all inert gases, those of groups 1 and 2 are all metals, and so are all those of group 3 except boron. With this exception, the non-metals are all contained in groups 4, 5, 6 and 7, and the most active non-metals stand at the top for, in a sub-group composed of non-metals, the non-metallic properties decrease with increase of atomic weight. This is well shown by the fact that no non-metal is known having a higher atomic weight than that of tellurium (Te = 127.5). In a sub-group of metals, the reverse is usually true—the higher the atomic weight the more marked the metallic properties.

ARRANGEMENT OF THE ELEMENTS ACCORDING TO THE PERIODIC LAW

	GROUP 0 Argon Group	GROUP 1 Sodium Group Cop. Group	GROUP 2 Calcium Group Zinc Group	GROUP 3 Aluminium Group	GROUP 4 Carbon Group	GROUP 5 Nitrogen Group	GROUP 6 Oxygen Group	GROUP 7 Halogen Group	GROUP 8 Including the Iron Group and the Platinum Group		
1st Short Period	He 4	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19			
2nd Short Period	Ne 20	Na 23	Mg 24	Al 27	Si 28.5	P 31	S 32	Cl 35.5			
1st Long Period	Ar 40	K 39 Cu 63.5	Ca 40 Zn 65.5	Sc 44 Ga 70	Ti 48 Ge 72	V 51 As 75	Cr 52 Se 79	Mn 55 Br 80	Fe 56	Co 59	Ni 58.7
2nd Long Period	Kr 82	Rb 85 Ag 108	Sr 87.5 Cd 112	Y 89 In 115	Zr 91 Sn 119	Cb 94 Sb 120	Mo 96 Te 127.5	I 127	Ru 102	Rh 103	Pd 106
3rd Long Period	X 128	Cs 133	Ba 137	La 139	Er 166			Sa 150			
4th Long Period		Au 197	Hg 200	Yb 173 Tl 204	Pb 207	Ta 181 Bi 208	W 184		Os 191	Ir 193	Pt 195
			Ra 226		Th 233		U 238				

The sodium group contains those elements which, from the chemical point of view, manifest metallic properties in the greatest perfection. The most positive metal of these, and, in fact, the most active metal known, is caesium ($Cs = 133$), which has the highest atomic weight in the group.

502. Prediction of Elements.—The student will notice at once that there are many gaps in the table. A gap arises when we are forced to leave a vacant space for the sake of preserving the arrangement. Thus, in the second long period, after molybdenum ($Mo = 96$) in the sixth group, the next known element in order of increasing atomic weight, is ruthenium ($Ru = 102$). Now the whole chemical character of this element shows that it belongs in the eighth group, and not under manganese. Further, if we simply proceeded in order, placing ruthenium under manganese, not only ruthenium itself but every following element would be thrown out of place, and the whole latter portion of the table would be disarranged. Therefore we leave a vacant space and preserve the arrangement, believing that the place under manganese belongs to some unknown element, which has an atomic weight of about 100. Thirty years ago, when the table was first published, gaps were more numerous. The Russian chemist *Mendelejeff*, the originator of the periodic law, gave it as his opinion that the vacant spaces would be filled by the discovery of new elements. In several cases he predicted in detail the properties of these elements and their principal compounds, from the place which they ought to occupy in the table. These predictions were verified, the properties of the newly discovered elements agreeing with Mendelejeff's statements with wonderful closeness—a striking proof that the periodic classification is a real law of nature and not a mere artificial arrangement.

503. Method of Prediction.—The method employed by Mendelejeff in predicting the properties of undiscovered elements will be made clear by an imaginary example. Suppose that *sodium* was unknown. There would then be a vacant space in the periodic table in group 1, between lithium and potassium. In the horizontal series, the gap would occur in the 2nd short period, between neon and magnesium.

The atomic weight of the unknown element should be approximately the mean of its two vertical neighbors:

$$\begin{array}{r} \text{Li} = 7 \\ \text{K} = 39 \\ \hline 2)\ 46 \\ \hline 23 \end{array}$$

or, the mean of its two horizontal neighbors:

$$\begin{array}{r} \text{Ne} = 20 \\ \text{Mg} = 24 \\ \hline 2)\ 44 \\ \hline 22 \end{array}$$

Since, in this family, the melting-point falls with increasing atomic weight, the melting-point of the unknown element will be somewhere between that of lithium (186°) and that of potassium (63°). We predict roughly that the unknown element would melt at a temperature not far from 100°.

Its physical and chemical properties would resemble those of lithium and potassium. It would be soft enough to be cut with a knife, would burn readily when heated, and would communicate a marked color to the flame of the Bunsen burner. It would lose its luster instantly in moist air and interact rapidly with water, liberating hydrogen and forming a hydroxide, which would be an active base.

The working out of the further details of the prediction may be left as an exercise to the student. It can be extended to the prediction of the properties not only of the unknown element, but also of its compounds.

504. Defects of the Periodic Arrangement.—The periodic arrangement is far from perfect. The upper portion of the table, as far down as lanthanum (La = 139), is substantially complete. There is only one vacancy, which belongs to an undiscovered metal in group 7, whose atomic weight will be about 100. Its horizontal neighbors are molybdenum (Mo) and ruthenium (Ru), and it will resemble manganese.

But after we leave lanthanum, the vacant places become so numerous that the latter portion of the table is quite fragmentary. Of course, there is not the slightest reason to believe that all of the elements have been discovered and investigated. It is possible that all these gaps will be filled by the results of future research.

Another difficulty is that *hydrogen* finds no place in the table. The student can find no better way of testing his knowledge of the table than to attempt to fit hydrogen into it. He will find it impossible to place it in any of the eight groups. The entire omission of an element of such importance, and of such unique chemical properties, is a serious defect in the table.

A further complication is that, in three cases, an element has a slightly *smaller* atomic weight than the one which precedes it in the table. The pairs of elements in which this curious contradiction occurs are the following:

Argon (Ar = 40) — Potassium (K = 39)
Cobalt (Co = 59) — Nickel (Ni = 58.7)
Tellurium (Te = 127.5) — Iodine (I = 127)

The properties of these elements are such that it is impossible to follow the order of increasing atomic weights without putting each element of the pair in a group in which it would be very much out of place. Thus, if we followed the order of increasing atomic weights we should have to place potassium with the inert gases and argon with the sodium metals, which would be a most unreasonable classification.

The periodic law is not a complete and perfected classification of the elements. It is still in its formative stage. In pointing out profitable subjects for research, and in fixing the true values of the atomic weights, it has been of great value to our science. The future will probably modify it in important details, but the fundamental fact that the properties of the elements are periodic functions of their atomic weights will remain.

CHAPTER XXX

CHEMICAL CALCULATIONS

NOTE TO TEACHERS.—The time allotted to chemistry in most schools will not permit the teacher to give all of the following problems, or even half of them, to his class. The author has attempted to supply a sufficient number of problems, of various degrees of difficulty, so that each teacher can choose those which suit the special needs of his students. Some of the problems are too difficult for many beginners. There are, however, in every class, students with a special aptitude for this work, who solve simple problems without much effort, and who lose interest in the subject unless something worthy of their ability is provided.

NOTE TO STUDENTS.—Use the **approximate atomic weights** in solving all problems.

505. Calculation of the Effect of Temperature, Pressure, and Water Vapor on the Volumes of Gases.—1. *Temperature.*—The *absolute temperature* is the temperature measured from 273° below 0° C. Thus, the absolute temperature of 10° is $273 + 10 = 283°$.

The absolute temperature of $-10°$ is $273-10 = 263°$.

Problem

1. Calculate the absolute temperature corresponding to the following centigrade temperatures:

a. 13°. *b.* 274°. *c.* —50°. *d.* —273°.

The volume of a mass of gas is directly proportional to its absolute temperature.

$$\text{New volume} = \text{Old volume} \times \frac{\text{New abs. temperature}}{\text{Old abs. temperature}}$$

In words, this means if we know the volume of a mass of gas at some known temperature, we can calculate its volume at some other temperature by multiplying the old volume by the new temperature, and dividing by the old temperature, both temperatures being absolute.

Never make the error of using ordinary centigrade temperatures, instead of absolute temperatures. It is easy to see that this leads directly to absurd results. For instance: I have a liter of gas at 0° C. What will its volume become at 273° C.?

Here, if we use ordinary centigrade degrees, the volume becomes

$$1 \times \frac{273}{0};$$

that is, the volume is infinite—which is absurd. But if we employ absolute degrees, the volume is

$$1 \times \frac{546}{273} = 2 \text{ liters;}$$

which is the correct result.

Problems

2. What volume will a liter of air at 0° C. occupy at 100° C.?

3. 5 l. of oxygen at 0° C. occupy what volume (*a*) at 10° C.? (*b*) at –10° C.?

4. 25 c.c. of nitrogen at 15° C. will measure what at the standard temperature, 0° C.?

5. I have 500 c.c. of hydrogen at 13° C. What will the volume become at 65° C.?

6. 600 c.c. of oxygen at 28° C. will measure what at –14° C.?

7. 500 l. of air at 20° C. will occupy what volume at 80° C.?

8. A liter of steam at 100° C. will occupy what volume at 120° C.?

9. 67 l. of air are heated from –30° C. to 60° C.? What is the new volume?

Since the volume of a mass of gas varies with the temperature, it is always necessary, in measuring gases, to know the temperature of the gas measured. And it is clear that the expression "1 liter of oxygen" has no meaning unless some particular temperature is either stated or understood. Now, in order to avoid the necessity of continually stating the temperature, it is extremely convenient to assume some temperature as a standard point which is to be understood unless some other temperature is stated. *The standard temperature universally agreed upon is* 0° *C.—the melting-point of ice.* Thus, when a writer speaks of "1 liter of oxygen" without stating the temperature under which the gas was measured, we know that 0° C. is meant.

The student should grasp the fact that every problem like those just solved is supposed to deal with a certain mass of gas which is not added to or subtracted from during the process of heating or cooling. Clearly, if temperature and pressure remain the same, the volume must be directly proportional to the weight of the gas. Thus, 1 gram of hydrogen at standard temperature and pressure occupies a volume of 11.2 liters. Evidently, 2 grams of hydrogen must measure 22.4 liters under the same conditions, and so on. But, in all problems of this sort, the quantity of gas is supposed to remain the same.

2. *Pressure.—The volume of a mass of gas is inversely proportional to the pressure upon it.* Usually the two pressures are stated in millimeters of mercury.

$$\text{New Volume} = \text{Old Volume} \times \frac{\text{Old Pressure}}{\text{New Pressure}}$$

That is, if the volume of a mass of gas is given at some pressure and it is required to calculate its volume at some other pressure, we must multiply the old volume by the old pressure and divide by the new pressure.

Problems

10. 10 l. of gas at a pressure of 743 m.m. will occupy what volume at 720 m.m.?

11. 18.5 c.c. of nitrogen are measured under a pressure of 745 m.m. What will the volume be at 760 m.m.?

12. A liter of oxygen is measured at 760 m.m. What will it measure at 748 m.m.?

13. 100 c.c. of air at 760 m.m. (1 atmosphere) will occupy what volume under 20 atmospheres?

14. What pressure is required to compress 500 c.c. of carbon dioxide at 728 m.m. to a volume of 400 c.c.?

15. What must the pressure be made in order to allow the 500 c.c. of gas of the preceding problem to expand to 850 c.c.?

In order not to be compelled to state continually the pressure, in speaking of the volumes of gases, and in order to be able to compare gas volumes, measured at different temperatures, with each other, 760 *m.m.* of *mercury is agreed upon as the standard pressure, which is understood when no pressure is stated.* This pressure is called 1 atmosphere, because the pressure of the air does not vary widely from that amount.

Since, as we have seen, 0° is the standard temperature, the expression "standard conditions" means 0° and 760 m.m. Thus, when a writer speaks of 1 liter of oxygen (or of any volume of any gas) without mentioning either temperature or pressure, we understand at once that the gas is supposed to exist at 0°, and under a pressure of 760 m.m. The abbreviation **STP** is often employed for standard temperature and pressure.

3. *When temperature and pressure both vary,* we have simply to correct for both, by the methods already studied. This can be done in two separate calculations, but it is easier and better to unite both corrections in one operation. The volume of a gas is directly proportional to the absolute temperature, and inversely proportional to the pressure.

Therefore

$$\text{New Volume} = \text{Old Volume} \times \frac{\text{New abs. temp.}}{\text{Old abs. temp.}} \times \frac{\text{Old Pressure}}{\text{New Pressure}}$$

In words, this means that in order to calculate the new volume of a gas at some new temperature and pressure, *we must multiply the old volume by the new absolute temperature and the old pressure, and divide it by the old absolute temperature and the new pressure.*

Such calculations can be rapidly, easily and correctly made by the use of *logarithms,* and this is true of chemical calculations generally. A table of logarithms is given for this purpose, and its use will save about half the time and labor of chemical calculations, and will greatly reduce the number of errors in the numerical work.

Problems

16. 100 c.c. of oxygen at 15° C. and 740 m.m. will occupy what volume at standard conditions?

$$\text{New Volume} = 100 \times \frac{273}{288} \times \frac{740}{760} = 92.3 \text{ c.c.}$$

NOTE.—The student will find that his chief difficulty in solving problems like this and the following ones is in determining which temperature and pressure to put in the numerator and which in the denominator. It will pay to make it a rule to inspect the fractions with great care before working out the calculation. Errors can be detected by the exercise of a little common sense. For instance, in the preceding problem the gas is to be cooled from 15° C. to 0° C. This will *reduce* its volume. Hence, the temperature-fraction must be $\frac{273}{288}$, not $\frac{288}{273}$. Also, the pressure is to be raised from 740 to 760, and this also will *reduce* the volume. Hence, the pressure-fraction must be $\frac{740}{760}$, not $\frac{760}{740}$.

17. Supposing the initial temperature in the preceding problem to be −15° C. instead of 15° C., what would be the new volume? The other figures remain the same.

18. What volume will 48 c.c. of nitrogen at standard conditions occupy at 18° C. and 733 m.m.?

19. 25 l. of a gas at standard conditions are cooled to −10° C., and the pressure reduced to 723 m.m. What is the new volume?

20. 310 c.c. of hydrogen at 10° C. and 530 m.m. will occupy what volume at 18.7° C. and 590 m.m.?

21. 1,704 c.c. of nitrogen at 11° C. and 760 m.m. are brought to a temperature of 27° C. and a pressure of 900 m.m. What is the volume?

22. 271 c.c. of hydrogen at 269° and 900 m.m. are cooled to −51° C., and the pressure decreased to 666 m.m. Calculate the final volume.

4. *The effect of water vapor on the volume of a mass of gas.*—Suppose that we have 100 c.c. of dry oxygen confined over mercury in a graduated tube. Let us admit a drop of water

and allow the oxygen to saturate itself with moisture. Clearly, the volume of gas in the tube must increase, for the water vapor will occupy space. The result is the same as though we had introduced a little nitrogen or some other gas into the tube, and allowed it to mix with the oxygen.

The volume can be kept 100 c.c. by increasing the pressure under which the gas is measured. But if this is done, the total pressure cannot be considered as exerted upon the oxygen in the tube, for the water vapor is also present. Hence, the pressure under which the gas really exists, and is measured, is *less* than the total pressure. How much less?

The pressure which saturated water vapor exerts at various temperatures is given in the table. When a gas is measured *over water*, or when it is measured saturated with water, the *pressure which water vapor exerts at the temperature of measurement must be ascertained from the table and deducted from the total pressure. The remainder will be the pressure under which the gas is really measured.*

VAPOR PRESSURE OF WATER

Temperature, Centigrade.	Vapor pressure in m.m. of mercury.	Temperature, Centigrade.	Vapor pressure in m.m. of mercury.	Tempera ture, Centigrade.	Vapor pressure in m.m. of mercury.
—10	2.09	12	10.46	26	24.99
— 5	3.11	13	11.16	27	26.51
0	4.60	14	11.91	28	28.10
+ 1	4.94	15	12.70	29	29.78
2	5.30	16	13.54	30	31.55
3	5.69	17	14.42	35	41.83
4	6.10	18	15.36	40	54.91
5	6.53	19	16.35	50	91.98
6	7.00	20	17.39	60	148.79
7	7.49	21	18.50	70	233.09
8	8.02	22	19.66	80	354.64
9	8.57	23	20.89	90	525.45
10	9.17	24	22.18	100	760.00
11	9.79	25	23.55		

The vapor pressure of water for a temperature not given in the table can easily be found by calculation. Thus, suppose it is required to find the vapor pressure for the temperature of 32.5°. The increase in vapor pressure from 30° to 35° is $41.83 - 31.55 = 10.28$ m.m. Hence, the increase from 30° to 32.5° will not be far from $10.28 \times \frac{2.5}{5}$, or 5.14 m.m., and the vapor pressure for 32.5° will be about 36.69 m.m. It will not be exactly 36.69 m.m., because, in the calculation, it is assumed that the vapor pressure increases proportionally with the temperature, which is not the case, but for small differences of temperature the error is small.

Problems

23. A mass of air at 15.3° C. and 747.2 m.m., measured *over water*, occupied a volume of 82.4 c.c. What volume would it occupy dry and at standard conditions?

Solution: From the table we observe that water vapor at 15° C. exerts a pressure of 12.7 m.m. and at 16° C. a pressure of 13.54 m.m. Hence its pressure at 15.3° C. must = 12.9 m.m.

The pressure under which the gas is really measured is

$$747.2 - 12.9 = 734.3 \text{ m.m.}$$

The rest of the calculation is the same as in the preceding problems:

$$82.4 \times \frac{273}{288.3} \times \frac{734.3}{760} = 75.39 \text{ c.c.}$$

24. 11.41 c.c. of a mixture of oxygen and hydrogen are measured over water at 14° C. and 743 m.m. Calculate the volume under standard conditions.

25. 112.1 c.c. of nitrogen saturated with water at 16° C. and 744 m.m. will occupy what volume dry and under standard conditions?

26. The gas-holder of a gas-works contains 4,500 cu. m. of illuminating gas, confined over water. The temperature is 9° C. and the pressure 776 m.m. How many cubic meters would the gas measure under standard conditions?

27. 100 c.c. of oxygen are confined over water and measured at 14° C. and 756 m.m. What will be the volume when the gas is dried and placed under standard conditions?

28. A gas-holder contains 10 l. of air confined over water at 20° C. and 756 m.m. What will the gas measure when dried, other conditions remaining the same?

506. Calculation of the Percentage Composition from the Formula (p. 89).—Let it be required to calculate the percentages of iron and sulphur in *pyrite*. The formula FeS_2 informs us that the pure mineral contains 56 parts by weight of iron and 64 of sulphur in 56 + 64 or 120 parts by weight. Hence the percentage of iron must be:

$\frac{56}{120} \times 100 = 46.67$ per cent., and that of sulphur,

$\frac{64}{120} \times 100 = 53.33$ per cent.

Problems

Calculate the percentage composition of the following substances. The amount of each element should be obtained by an independent calculation—never by subtracting the sum of the others from 100. State the result to two decimal places. If the third decimal place is greater than 5, add 1 to the second; if less than 5, discard it. Check the results by ascertaining whether the sum of the percentages for each compound equals 100. Use the *approximate* atomic weights in all problems.

29. Mercuric oxide, HgO.
30. Mercuric chloride, $HgCl_2$.
31. Potassium chlorate, $KClO_3$.
32. Manganese dioxide, MnO_2.
33. Potassium nitrate, KNO_3.
34. Water, H_2O.
35. Mercurous chloride, $HgCl$.
36. Sodium chloride, $NaCl$.
37. Nitric acid, HNO_3.
38. Sugar, $C_{12}H_{22}O_{11}$.

Calculate the percentage of *water* only in the following:

39. Copper sulphate, $CuSO_4\,5H_2O$.
40. Potassium alum, $K_2SO_4Al_2(SO_4)_324\ H_2O$.
41. Chrome alum, $K_2SO_4Cr_2(SO_4)_3\ 24\ H_2O$.
42. Ferrous sulphate, $FeSO_4\ 7\ H_2O$.
43. Calculate the percentage of iron in the following important iron ores:

Hematite, Fe_2O_3; magnetite, Fe_3O_4; Siderite, $FeCO_3$; Limonite, $2\ Fe_2O_3\ 3\ H_2O$.

507. Calculation of the Formula from the Percentage Composition (p. 90).—Let it be required to obtain the formula of *copper glance*. The mineral contains:

Sulphur 20.13 per cent.
Copper 79.87 per cent.
Total 100 per cent.

Divide the percentage of sulphur by the atomic weight of sulphur:

$$20.13 \div 32 = 0.629.$$

Divide the percentage of copper by the atomic weight of copper:

$$79.87 \div 63.5 = 1.258.$$

The molecule of the mineral therefore contains copper and sulphur atoms in the proportions 1.258 : 0.629. But 1.258 : 0.629 : : 2 : 1, hence the simplest formula of copper glance is Cu_2S. The slight errors which always exist in percentages determined by chemical analysis do not interfere with the calculation.

Problems

Calculate the simplest formulas of the following:

44. Hydrogen 2.74 per cent.
Chlorine 97.26 per cent.

45. Nitrogen 30.43 per cent.
Oxygen 69.57 per cent.

46. Carbon 40.00 per cent.
Hydrogen 6.67 per cent.
Oxygen 53.33 per cent.

47. Mercury 44.07 per cent.
Iodine 55.93 per cent.

48. Calcium 40.00 per cent.
Carbon 12.00 per cent.
Oxygen 48.00 per cent.

49. Potassium 52.35 per cent.
Chlorine 47.65 per cent.

50. Potassium 45.9 per cent.
Nitrogen 16.5 per cent.
Oxygen 37.6 per cent.

51. Silver 56.40 per cent.
Chlorine 18.52 per cent.
Oxygen 25.08 per cent.
If silver is univalent, what must be the formula of *chloric acid*?

52. Sodium 32.9 per cent.
Aluminium 12.9 per cent.
Fluorine 54.2 per cent.
(52) is the mineral *cryolite*.

53. Sulphur 35.87 per cent.
Copper 34.40 per cent.
Iron 30.47 per cent.
(53) is *chalcopyrite*. This is an actual analysis, and the percentages do *not* add to 100.

508. Calculations of Weights—(p. 91).

54. How many grams of mercury and how many of oxygen can be obtained by heating 25 g. of mercuric oxide?

$$HgO \longrightarrow Hg + O$$

55. How many grams of oxygen can be obtained by heating 10 g. of potassium chlorate?

$$KClO_3 \longrightarrow KCl + 3\,O$$

56. How many grams of potassium chlorate are needed to prepare 12 g. of oxygen?

57. What is the weight of the hydrogen which escapes when 0.5 g. of sodium acts upon water?

$$Na + H_2O \longrightarrow NaOH + H$$

58. What is the cost of preparing a kilogram of hydrogen from zinc and sulphuric acid? Suppose that the price of zinc is 44 cts. per kilo. and that of sulphuric acid 6 cts. per kilo.

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

59. How many grams of zinc oxide are produced by burning 5 g. of zinc?

$$Zn + O \longrightarrow ZnO$$

60. How many grams of magnesium oxide are produced by burning 12 g. of magnesium ribbon?

$$Mg + O \longrightarrow MgO$$

61. What is the least weight (in grams) of phosphorus that will completely remove the oxygen from 200 c.c. of air? Assume that air contains 21% of oxygen by volume or 23% by weight. Weight of 1 liter of oxygen = 1.43 grams.

$$2\,P + 5\,O \longrightarrow P_2O_5$$

62. How many grams of copper wire can be changed to cupric oxide by heating in a liter of air?

$$Cu + O \longrightarrow CuO$$

63. What would be the increase in weight of 30 g. of powdered iron if converted (*a*) into ferrous oxide FeO; (*b*) into ferric oxide Fe_2O_3?

64. How many grams of potassium chlorate are necessary to furnish enough oxygen to convert 30 g. of copper into cupric oxide?

65. How many grams of oxygen can be obtained by the catalytic action of platinum upon 100 g. of a 5% solution of hydrogen peroxide?

$$H_2O_2 \longrightarrow H_2O + O$$

66. How many grams of pure hydrogen peroxide will convert 10 g. of lead sulphide into lead sulphate?

$$PbS + 4\,H_2O_2 \longrightarrow PbSO_4 + 4\,H_2O$$

67. How many grams of ammonium chloride are necessary to prepare 3 kg. of a 30% ammonia solution?

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

68. How many grams of nitrous oxide can be made by heating 20 g. of ammonium nitrate?

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

69. How many kilograms of a 30% solution of hydrochloric acid can be made from 50 kg. of sodium chloride?

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl$$

70. How many grams of potassium bromide and how many of silver nitrate are needed to prepare 12 g. of silver bromide?

$$AgNO_3 + KBr \longrightarrow AgBr + KNO_3$$

71. How many grams of bromine are needed to make half a kilogram of potassium bromide? Assume that all the bromine is finally obtained as KBr.

72. How many grams of sodium bromide must be heated with sulphuric acid and manganese dioxide to obtain 10 g. of bromine?

$$2\,NaBr + MnO_2 + 3\,H_2SO_4 \longrightarrow 2\,Na\,HSO_4 + MnSO_4 + 2\,H_2O + Br_2$$

73. 5 g. of sulphur are burned with an excess of air and the combustion products passed over finely divided platinum. How many grams of sulphur trioxide are produced.

$$S + O_2 \longrightarrow SO_2$$
$$SO_2 + O \longrightarrow SO_3$$

74. 80 g. of a solution of sulphuric acid are exactly sufficient to dissolve 22 g. of cupric oxide. What was the percentage by weight of sulphuric acid in the original solution?

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

75. 30 kg. of a phosphate rock, which contains 58% of tri-calcium phosphate, $Ca_3(PO_4)_2$, are heated in an electric furnace with sand and coke. How many grams of phosphorus are obtained?

$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C \longrightarrow 3\,CaSiO_3 + 5\,CO + 2\,P$$

76. 50 kg. of impure stibnite containing 60% of Sb_2S_3 are heated with iron. How many kilograms of antimony are obtained?

$$Sb_2S_3 + 3\,Fe \longrightarrow 3\,FeS + 2Sb$$

77. 310 g. of borax-crystals are dissolved in a small quantity of water and sulphuric acid is added. How many grams of sulphuric acid should be used and how many grams of boric acid are obtained?

$$Na_2B_4O_7 10\,H_2O + H_2SO_4 \longrightarrow Na_2SO_4 + 4\,H_3BO_3 + 5\,H_2O$$

78. I have 100 kg. of tin ore containing 3% of tin dioxide. How many grams of tin can be obtained from it, assuming that 5% of the tin is lost during the extraction?

$$SnO_2 + C \longrightarrow Sn + CO_2$$

79. How many grams of tin and how many of a 30% solution of hydrochloric acid are needed to prepare 100 g. of crystallized stannous chloride $SnCl_2\ 2H_2O$?

$$Sn + 2\,HCl + 2\,H_2O \longrightarrow SnCl_2\ 2\,H_2O + H_2$$

80. How many kilograms of potassium nitrate can be made from a metric ton of sodium nitrate and how many kilograms of potassium chloride must be used? A metric ton = 1000 kg.

$$NaNO_3 + KCl \longrightarrow NaCl + KNO_3$$

81. Calculate the loss in weight when 15 g. of pure marble are heated until the chemical change is complete.

$$CaCO_3 \longrightarrow CaO + CO_2$$

82. An excess of barium chloride solution was added to 32 g. of a solution of sulphuric acid. The barium sulphate obtained weighed 11.43 g. Calculate the percentage of sulphuric acid in the sulphuric acid solution.

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\,HCl$$

83. 1.4 g. of an alloy of copper and silver were dissolved in nitric acid and hydrochloric acid was added. The silver chloride AgCl, which was precipitated, weighed 1.6 g. How many grams of silver and copper were present in the sample and what was its percentage composition?

84. How many kilograms of a 10% solution of acetic acid can be made from 10 kg. of 80% alcohol?

$$C_2H_6O + O_2 \longrightarrow C_2H_4O_2 + H_2O$$

85. Calculate the percentages of carbon and hydrogen in the first five members of the methane series of hydrocarbons. Their general formula is C_nH_{2n+2}.

86. *Anhydrous* sodium carbonate has the formula Na_2CO_3. If 10g. of the *crystallized* salt lose 6.29 g. of water on the application of heat, how many molecules of water of crystallization were present?

87. *Anhydrous* barium chloride is $BaCl_2$. If 5 g. of the *crystallized* salt leave, after being heated, a residue of 4.26 g., how many molecules of water of crystallization were present?

88. Anhydrous zinc sulphate is $ZnSO_4$. If the *crystallized* salt loses 43.8% of its weight when heated, what is its formula?

89. Mercuric oxide is heated (*a*) alone; (*b*) with carbon; (*c*) with hydrogen. Calculate the weight of all the products if 10 g. of mercuric oxide were used.

$$\begin{aligned}&(a)\ HgO \longrightarrow Hg + O\\&(b)\ 2\,HgO + C \longrightarrow 2\,Hg + CO_2\\&(c)\ HgO + H_2 \longrightarrow Hg + H_2O\end{aligned}$$

90. How many grams of chlorine can be obtained by the electrolysis of a solution containing 100 g. of sodium chloride?

91. The hydrogen obtained by dissolving 12.1 g. of zinc in hydrochloric acid is passed over warm mercuric oxide. How many grams of water and how many of mercury are produced?

$$\begin{gathered}Zn + 2HCl \longrightarrow ZnCl_2 + H_2\\HgO + H_2 \longrightarrow H_2O + Hg\end{gathered}$$

92. How many grams of ammonium nitrate would yield enough nitrous oxide to burn 24 g. of carbon?

$$\begin{gathered}NH_4NO_3 \longrightarrow N_2O + 2H_2O\\C + 2\,N_2O \longrightarrow CO_2 + 2\,N_2\end{gathered}$$

509. Volumes.—The gases are at S.T.P. unless otherwise stated.

How many liters of hydrogen are produced when 32.75 grams of zinc are dissolved in sulphuric acid?

$$\underset{65.5\text{ grams.}}{Zn} + H_2SO_4 \longrightarrow ZnSO_4 + \underset{22.4\text{ liters}}{H_2,}$$

hence: $65.5 : 32.75 :: 22.4 : x \quad x = 11.2$ liters

93. How many liters of hydrogen are formed by the action of 3 grams of sodium upon water?

$$Na + H_2O \longrightarrow NaOH + H$$

94. How many grams of zinc and how many of 90% suphuric acid are needed to fill with hydrogen a gas holder of 15 l. capacity?

95. How many liters of a mixture of hydrogen and oxygen are formed by the electrolysis of 20 g. of water?

96. A liter of the mixed gases of (95) is exploded. How many cubic centimeters of water at 4° are obtained?

97. How many grams of water result from the burning of 12 l. of hydrogen? 12

98. How many times denser is liquid water than hydrogen gas? 12
1 l. hydrogen = 0.09 g.

99. How many times denser is copper than hydrogen? Specific gravity of copper = 8.9.

100. A solution of hydrochloric acid was made by dissolving 450 l. of hydrogen chloride in one liter of water. What was the percentage by weight of hydrogen chloride in the solution?

101. How many grams of alcohol and how many liters of carbon dioxide result from the fermentation of a kilogram of grape sugar?

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_6O + 2\,CO_2$$

102. How many liters of oxygen can be made by heating 50 g. of mercuric oxide?

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

103. How many cubic centimeters of oxygen are obtained by heating one gram of potassium chlorate?

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

104. How many grams of mercuric oxide are needed to prepare 12 liters of oxygen?

105. How many kilograms of oxygen and how many of nitrogen are contained in a room 8 meters long, 6 meters wide, and 4 meters high? Assume 23% by weight of oxygen in air. Take the balance as nitrogen. Weight 1 liter air = 1.293 grams.

106. A certain blast furnace requires daily 600,000 kilograms of air. How many cubic meters at S.T.P. does this make?

107. How many liters of oxygen are required to burn 1 g. of pure charcoal and how many liters of carbon dioxide result?

$$C + O_2 \longrightarrow CO_2$$

108. How many grams of water are formed by the burning of 5 l. of hydrogen?

109. How many liters of hydrogen must be burned to produce 5 g. of water?

110. How many liters of air are necessary to burn a kilogram of a coke which contains 82% of carbon?

111. How many liters of nitrous oxide can be made by heating 75 g. of ammonium nitrate?

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

112. How many liters of hydrogen chloride can be made from 25 g. of sodium chloride?

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl$$

113. How many grams of salt must be electrolyzed to yield 10 l. of chlorine?

114. How many grams of ammonium chloride are needed to furnish 10 l. of hydrogen chloride?

$$2\,NH_4Cl + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 2\,HCl$$

115. If a sample of bleaching powder liberates, when treated with acids, 32% of its weight of chlorine, how many liters of chlorine, Cl_2, can be obtained from a kilogram?

116. How many grams of phosphorus are needed to remove all the oxygen from a cubic meter of air? Air contains 23% oxygen by weight. 1 l. air weighs 1.293 g.

$$2\,P + 5\,O \longrightarrow P_2O_5$$

117. How many liters of hydrogen sulphide can be obtained from 150 g. of a sample of iron sulphide which contains 60% FeS?

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

118. The capacity of a room is 160 cu. m. and the air in it contains 0.03% of hydrogen sulphide. How many liters of chlorine are necessary to destroy the odor?

$$H_2S + Cl_2 \longrightarrow 2\,HCl + S$$

119. How many liters of sulphur dioxide are produced when 12 grams of sulphur are burned?

$$S + O_2 \longrightarrow SO_2$$

How many liters of oxygen are necessary?

120. A metric ton (1000 kg.) of pyrite containing 7% of foreign substances is burned in a lead-chamber plant. How many kilograms of ferric oxide does the residue contain, and how many liters of sulphur dioxide are produced? How many kilograms of 62% chamber acid can be obtained?

$$2\,FeS_2 + 11\,O \longrightarrow Fe_2O_3 + 4\,SO_2$$
$$SO_2 + H_2O + O \longrightarrow H_2SO_4$$

121. How many grams of bromine can be obtained by passing chlorine into 6 kg. of a liquid containing 0.25% by weight of magnesium bromide? How many liters of chlorine are necessary?

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$$

122. How many grams of iodine can be obtained by leading chlorine into 1 kg. of a solution containing 1% by weight of potassium iodide? How many liters of chlorine are needed?

$$2\,KI + Cl_2 \longrightarrow 2\,KCl + I_2$$

123. How many liters of hydrofluoric acid can be made from 20 g. of fluor-spar?

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,HF$$

124. How many cubic centimeters of acetylene can be prepared from 10 g. of 90% calcium carbide?

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

125. How many cubic meters of air are needed to burn a metric ton of anthracite coal which contains 95% of carbon? Air contains 21% oxygen by volume.

$$C + O_2 \longrightarrow CO_2$$

126. How many grams of water and how many liters of carbon dioxide are produced by burning 2 l. of methane?

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

510. Volumes at Temperatures and Pressures other than Standard.—How many liters of oxygen at 27° and under a pressure of 740 m.m. can be made by heating 27 grams of mercuric oxide?

$$\underset{432 \text{ grams}}{2\,HgO} \longrightarrow 2\,Hg + \underset{22.4 \text{ liters}}{O_2}$$

Hence, for the volume of the oxygen at S.T.P. we have:

$$\frac{22.4 \times 27}{432}$$

This must now be corrected for temperature and pressure. The absolute temperature of 27° is 273° + 27° = 300°. For the final volume we have:

$$22.4 \times \frac{27}{432} \times \frac{300}{273} \times \frac{760}{740} = 1.58 \text{ liters}$$

The use of four-place logarithms greatly simplifies the calculation.

127. How many liters of sulphur dioxide at 15° and 860 m. m. are produced by burning 8 g. of sulphur?

$$S + O_2 \longrightarrow SO_2$$

128. How many liters of carbon dioxide at 15° and 760 m.m. are produced by burning 6 g. of pure carbon?

$$C + O_2 \longrightarrow CO_2$$

129. How many liters of nitrous oxide at 15° and 800 m.m. can be obtained by heating 400 g. of ammonium nitrate?

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

130. How many liters of ammonia at 15° and 380 m.m. can be obtained from 40 g. of ammonium chloride?

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

131. How many liters of air measured at 20° and 760 m.m. are required to burn 10 g. of pure carbon?

$$C + O_2 \longrightarrow CO_2$$

132. How many liters of hydrogen sulphide measured at 16°.5 and 754 m.m. are produced when 250 g. of iron sulphide are dissolved in hydrochloric acid?

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

133. How many liters of ammonia at 15° and 748 m.m. are produced by heating 100 g. of sal ammoniac with slaked lime?

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

134. How many grams of pure sal ammoniac and how many grams of 92% sodium nitrite are needed to liberate 5 l. of nitrogen at 12°.5 and 765 m.m.?

$$Na\,NO_2 + NH_4\,Cl \longrightarrow Na\,Cl + 2\,H_2O + N_2$$

135. How many liters of nitrous oxide at 15° and 700 m.m. can be obtained by heating 200 g. of ammonium nitrate?

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

136. How many liters of nitric oxide at 15° and 740 m.m. can be obtained by dissolving 80 g. of copper in nitric acid?

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

137. A piece of pure marble weighing 10 g. is heated to complete decomposition. (*a*) How many grams of lime remain? (*b*) How many liters of carbon dioxide at 20° and 740 m.m. escape?

$$CaCO_3 \longrightarrow CaO + CO_2$$

138. How many liters of carbon dioxide at 12° and 750 m.m. are produced by dissolving 20 grams of pure marble in hydrochloric acid?

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

511. Simple Calculations of Atomic Weights.—*Berzelius* found that 10 g. of lead yielded 10.77 g. of lead monoxide, PbO. What is the atomic weight of lead?

The weight of oxygen which unites with 10 g. of lead is $10.77 - 10 = 0.77$ g.

The atomic weight is the number of grams of lead which in lead monoxide is united with 16 g. of oxygen. Hence we have:

$$0.77 : 10 :: 16 : x \qquad x = 207.9$$

1 g. of tin was converted into tin dioxide SnO_2. The increase in weight was 0.271 gram. What is the atomic weight of tin? The atomic weight is the number of grams of tin which, in tin dioxide, is combined with 32 g. of oxygen. Hence:

$$0.271 : 1 :: 32 : x \qquad x = 118$$

Stas found that 101.519 g. of silver, when heated in chlorine, gave 134. 861 g. of silver chloride, $AgCl$. Required, the atomic weight of silver.

The weight of chlorine which combined with the silver is $134.861 - 101.519 = 33.342$ g. Taking the atomic weight of chlorine as 35.5 we have:

$$33.342 : 101.519 :: 35.5 : x \quad x = 108.1$$

139. Dumas and Stas obtained 59.3765 g. of carbon dioxide, CO_2, by burning 16.192 g. of pure carbon. What is the atomic weight of carbon, if $O = 16$?

140. Berzelius oxidized 25 g. of lead and obtained 26.925 g. of lead monoxide, PbO. What is the atomic weight of lead?

141. Berzelius heated 43.9650 g. of lead monoxide in hydrogen and obtained 40.8125 g. of lead. What is the atomic weight of lead?

$$PbO + H_2 \longrightarrow Pb + H_2O$$

142. If 118.3938 g. of mercuric oxide, HgO, yield, when heated, 109.6308 g. of mercury, what is the atomic weight of mercury?

143. 88.5832 g. of mercuric sulphide, HgS, yield, when completely decomposed, 76.3725 g. of mercury. What is the atomic weight of mercury?

144. 0.5 g. of zinc, when dissolved in hydrochloric acid, liberated 183.7 c.c. of hydrogen measured over water at 15° and 760 m.m. What is the atomic weight of zinc, if H = 1.008?

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

145. If 1 g. of zinc set free 366 c.c. of hydrogen, measured over water at 9° and 748 m.m., what is the atomic weight of zinc?

146. The specific heat of lithium is 0.941, of potassium 0.166, of chromium 0.121, of iron 0.114, of cobalt 0.107, of nickel 0.108, of tin 0.054, of mercury 0.032 and of lead 0.031. Assuming that the product of specific heat and atomic weight is, in each case, 6.4, calculate the atomic weights of these metals. See Law of Dulong and Petit, p. 228.

Miscellaneous Problems

147. If 27.396 g. of water contain 24.352 g. of oxygen, what is the percentage composition of water?

148. 4 g. of hydrogen are slowly passed through a glass tube containing a large quantity of cupric oxide, heated to redness. (*a*) How many grams will this tube lose in weight? (*b*) How many grams of water will be formed?

149. 10.98 g. of a solution of potassium chlorate saturated at 18° were placed in a weighed dish and evaporated to dryness. The potassium chlorate which remained weighed 0.7025 g. How many grams of potassium chlorate were contained in 100 g. of the solution?

150. Using the figures of problem 149, calculate how many grams of potassium chlorate 100 g. of water at 18° will dissolve.

151. Using the same figures, calculate how many grams of water at 18° are needed to dissolve 1 g. of potassium chlorate.

152. A solution of table-salt saturated at 15° contained 26.39% of salt. How many grams of salt will 100 g. of water dissolve at 15°?

153. If 75 c.c. of oxygen could be changed completely to ozone, what volume of ozone could be obtained?

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

154. 115 c.c. of oxygen were partly converted into ozone. The volume contracted to 110 c.c., but, when the gas was gently heated, the original volume was restored. Calculate (*a*) the number of cubic centimeters of ozone which had been produced, and (*b*) its percentage by volume.

155. 160 c.c. of oxygen containing ozone were heated. The volume became 170 c.c. (*a*) How many c.c. of ozone, and (*b*) what percentage of it by volume, were present?

156. Calculate the percentage composition of (*a*) sodium carbonate Na_2CO_3; (*b*) crystallized sodium carbonate, $Na_2CO_3 10\ H_2O$. In (*b*) calculate *water*, not hydrogen.

157. How many grams of sodium are necessary to decompose 36 g. of water? How many grams of hydrogen are liberated?

$$Na + H_2O \longrightarrow NaOH + H$$

158. How many grams of sodium can be obtained by the electrolysis of 20 g. of sodium hydroxide?

$$NaOH \longrightarrow Na + O + H$$

159. A piece of sodium was placed in water. 500 c.c. of hydrogen, measured at S.T.P. escaped. What was the weight of the sodium?

160. How many grams of chlorine can be obtained by heating 12.5 g. of manganese dioxide?

$$MnO_2 + 4\ HCl \longrightarrow MnCl_2 + 2\ H_2O + Cl_2$$

161. How many grams of manganese dioxide are needed to make 25 g. of chlorine from hydrochloric acid?

162. How many grams of a hydrochloric acid solution containing 20% HCl are needed to liberate 100 g. of chlorine with manganese dioxide?

163. 20 c.c. of chlorine were mixed with 16 c.c. of hydrogen and the mixture exploded. What volumes of what gases remained in the vessel?

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

164. Hydrogen was burned in chlorine and the hydrogen produced collected. It weighed 146 g. How many grams of both gases had been consumed?

165. 50 g. of sodium hydroxide are dissolved in water and the solution mixed with a solution containing 50 g. of pure hydrochloric acid. What substances and how many grams of each are contained in the resulting liquid? Do not calculate *water*.

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

166. 32.75 g. of zinc are dissolved in hydrochloric acid. How many grams of zinc chloride and how many of hydrogen are produced?

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

167. 40 g. of magnesium are dissolved in hydrochloric acid. How many grams of hydrogen and how many of magnesium chloride are formed?

$$Mg + 2\ HCl \longrightarrow MgCl_2 + H_2$$

168. Determine the name and formula of a compound having the following composition:

Sodium	21.60
Chlorine	33.33
Oxygen	45.07

169. 25 g. of pure marble are dissolved in hydrochloric acid. How many grams of each product is formed? How many grams of hydrochloric acid, HCl, are consumed?

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

170. 2 g. of finely divided copper were heated in oxygen. 2.5063 g. of cupric oxide, CuO, were produced. Calculate the atomic weight of copper.

171. 16.7 c.c. of air were confined over mercury in a eudiometer and enough hydrogen added to make the volume 30 c.c. After explosion, the volume was 19.5 c.c. What percentage of oxygen by volume did the air contain?

172. 20 c.c. of air are mixed with 10 c.c. of hydrogen and the spark is passed. After the explosion, what volumes of what gases remain in the tube? Assume that air contains 21 per cent by volume of oxygen.

173. 2 l. of air were passed over hot copper. The increase in weight of the copper was .6 g. What was the percentage of oxygen by weight in the air? Assume the weight of 1 l. of air to be 1.293 g.

174. What weight of nitrogen can be obtained by heating 13.8 g. of sodium nitrate, $NaNO_2$, with the required quantity of ammonium chloride, NH_4Cl? How many grams of ammonium chloride are needed? What weights of salt and of water are formed? See problem 134.

175. 856 g. of ammonium chloride are heated with sodium hydroxide. How much ammonia by weight escapes?

$$NH_4Cl + Na\ OH \longrightarrow Na\ Cl + H_2O + NH_3$$

176. Calculate the percentage composition of:

a. Ammonium chloride, NH_4Cl.
b. Ammonium nitrate, NH_4NO_3.
c. Ammonium sulphate, $(NH_4)_2SO_4$.
d. Ammonium hydroxide, NH_4OH.

177. When a stream of electric sparks is passed through ammonia it is decomposed, two volumes yielding one volume of nitrogen and three volumes of hydrogen. What volumes of nitrogen and hydrogen are formed when 300 c.c. of ammonia are treated in this way?

178. 100 c.c. of ammonia are decomposed by a stream of sparks. (*a*) What volume of oxygen must be added to the resulting mixture to combine with the hydrogen and produce water? (*b*) After the water has condensed, what gas will remain in the tube, and how much?

179. 32 c.c. of ammonia are decomposed by sparks. 50 c.c. of oxygen are added, and the mixture is caused to explode. What volumes of what gases are left?

180. An unknown volume of ammonia is decomposed in a eudiometer, an unknown volume of oxygen is mixed with it, and the mixture exploded. After the explosion the contraction in volume is 18 c.c. and the tube still contains some oxygen. (*a*) What volume of ammonia was taken in the first place, and (*b*) what volume of nitrogen was left in the tube?

181. Ammonium chloride is heated in a flask with sodium hydroxide and the ammonia passed into 31.5 g. of pure nitric acid. How much ammonium chloride must be used in order to convert all the nitric acid into ammonium nitrate?

182. What weight of nitric acid containing 80 per cent. HNO_3 is necessary to dissolve 10 g. of cupric oxide?

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

183. What weight of pure nitric acid would contain 50 g. of oxygen?

184. Assuming that the density of pure nitric acid is 1.5, how many grams of oxygen do 3 l. of it contain?

185. How many grams of nitric acid can be obtained (*a*) by heating 200 kilos of sodium nitrate with sulphuric acid; (*b*) by heating 200 kilos of potassium nitrate with sulphuric acid?

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$
$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$

186. I require 120 g. of cupric oxide. How many grams of crystallized cupric nitrate must be heated to redness to make it?

$$Cu(NO_3)_2 3H_2O \longrightarrow CuO + 2\,NO_2 + O + 3\,H_2O$$

187. How many grams of nitric acid are needed to convert 400 g. of potassium hydroxide into potassium nitrate?

$$KOH + HNO_3 \longrightarrow KNO_3 + H_2O$$

188. Calculate the formula of a compound having the following composition:

9.09 per cent nitrogen;
20.77 per cent oxygen;
70.13 per cent silver.

189. Calculate the molecular weights of the following compounds:

a. Sugar, $C_{12}H_{22}O_{11}$;
b. Bismuth nitrate, $Bi(NO_3)_3$;
c. Nitroglycerin, $C_3H_5(NO_3)_3$;
d. Glucose, $C_6H_{12}O_6$.

190. What is the weight in grams of 28 l. (*a*) of nitrous oxide; (*b*) of nitric oxide?

191. What is the volume in liters (*a*) of 11 g. of nitrous oxide; (*b*) of 5 g. of nitric oxide?

192. How many liters of hydrogen are needed to form water with the oxygen (*a*) of 22 l. of nitrous oxide; (*b*) of 22 g. of nitrous oxide?

$$N_2O + H_2 \longrightarrow H_2O + N_2$$

193. What is the volume of 13 g. of nitric oxide?

194. How many liters of nitrous oxide—measured at standard conditions—can be made from 80 g. of ammonium nitrate? Solve by inspection.

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

195. How many grams of ammonium nitrate are needed to make 80 l. of nitrous oxide?

196. How many grams of ammonium nitrate are needed to make 4,000 c.c. of nitrous oxide?

197. How many grams of copper are needed to produce 30 l. of nitric oxide?

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

198. How many grams of ammonium nitrate are needed to produce 10 l. of nitrous oxide?

199. How many liters of nitrous oxide at 15° C. and 700 m.m. can be obtained by heating 100 g. of ammonium nitrate?

200. How many liters of nitric oxide at 13° and 740 m.m. is obtained by dissolving 40 g. of copper in nitric acid?

201. 10 g. of pure sodium hydroxide are dissolved in water. (*a*) How many grams of nitric acid must be added to make the solution neutral? (*b*) How many grams of sodium nitrate would be obtained if this was done?

202. I have a solution which contains just 40 g. of pure sodium hydroxide in 1 liter. Calculate the quantities by weight of (*a*) HCl, (*b*) HNO_3, and (*c*) H_2SO_4, which will be required to neutralize 1 c.c. of it.

203. 15.75 g. of nitric acid are mixed with 23.25 g. of sodium hydroxide, both dissolved in water. What two compounds does the solution contain and how many grams of each? Do not calculate *water*.

204. In ascertaining the strength of a dilute solution of HCl, 50 c.c. of it were measured out and neutralized with a solution of sodium hydroxide containing .003 g. of NaOH in 1 c.c. 40 c.c. of the sodium hydroxide solution was required. What weight of HCl was contained in 1 c.c. of the hydrochloric acid?

205. 30 c.c. of a solution of potassium hydroxide containing .01 g. of KOH in 1 c.c. was needed to neutralize 40 c.c. of a solution of HCl. How many grams of HCl did 15 c.c. of the hydrochloric acid solution contain?

206. 20 c.c. of a solution containing .005 g. of KOH in 1 c.c. just neutralized 20 c.c. of a solution of hydrochloric acid. How many grams of HCl did 15 c.c. of the latter contain?

207. How many grams of potassium are required to liberate from water enough hydrogen to combine with 3 g. of oxygen?

208. How many liters of oxygen are needed to combine with the hydrogen given off by the action of 9.75 g. of potassium on water?

209. How many grams of (*a*) potassium carbonate must be heated with how many grams of (*b*) pure charcoal to produce 9.75 g. of potassium, and (*c*) what volume of carbon monoxide would be liberated?

$$K_2CO_3 + 2\,C = 3\,CO + 2\,K$$

210. Calculate the percentage composition (*a*) of silver chloride, $AgCl$; (*b*) of silver sulphide, Ag_2S.

211. Calculate the formula of a compound of the following composition:

Silver	65.45
Sulphur	19.39
Arsenic	15.16

212. When hydrogen is heated with silver chloride, silver is produced:

$$AgCl + H = HCl + Ag$$

If 52.65 c.c. of hydrogen produce 0.505 g. of silver, what is the atomic weight of silver?

213. Calculate the percentage composition of silver acetate, $AgC_2H_3O_2$.

214. How many grams of zinc are required to precipitate 5 g. of silver from solution?

$$2\,\overset{+}{Ag} + Zn = \overset{++}{Zn} + 2\,Ag$$

215. A piece of pure marble weighing 50 g. is heated to complete decomposition. (*a*) What is the formula and weight of the substance which remains? (*b*) What gas escapes and what volume measured at 20° and 740 m.m. (p. 313)?

216. How many tons of limestone must be heated to make 200 tons of lime (p. 313)?

217. Calculate the percentage composition (*a*) of barium sulphate, $BaSO_4$; (*b*) of barium carbonate, $BaCO_3$.

218. 10 g. of barium carbonate are dissolved in hydrochloric acid. (*a*) What volume of carbon dioxide is produced, and (*b*) how many grams of crystallized barium chloride, $BaCl_2 2\,H_2O$, can be obtained from the solution?

219. How many grams of barium sulphate can be made from 2 g. of calcium sulphate, $CaSO_4$?

220. 1.182 g. of barium carbonate were dissolved in hydrochloric acid, and the solution precipitated with sulphuric acid. The barium sulphate obtained weighed 1.398 g. Calculate the percentage of barium in the barium carbonate.

221. What volume of oxygen is needed to burn 9 g. of magnesium to magnesium oxide MgO?

222. If 0.4 g. of magnesium liberated 391 c.c. of dry hydrogen at 13° when treated with HCl, what is the atomic weight of magnesium?

223. The electric current is passed through fused magnesium chloride, $MgCl_2$, until 14 g. of magnesium are obtained. What volume of chlorine at standard conditions is liberated (p. 219)?

224. 758 g. of mercuric chloride are dissolved in water. (*a*) How many grams of potassium iodide, KI, must be added to the liquid, and (*b*) how many grams of mercuric iodide, HgI_2, will be obtained?

225. If mercurous chloride contains 84.93 per cent. mercury and 15.07 per cent. chlorine, and if the formula is Hg_2Cl_2, what is the atomic weight of mercury?

226. If mercuric chloride has the formula $HgCl_2$ and contains 73.8 per cent. of mercury and 26.2 per cent of chlorine, what is the atomic weight of mercury?

227. Calculate the percentage composition of borax, $Na_2B_4O_7$-$10\,H_2O$. Calculate *water*, not hydrogen.

228. If 6.75 g. of aluminium, when dissolved in hydrochloric acid to $AlCl_3$, yield 8.4 l. of hydrogen, what is the atomic weight of the metal?

229. If 50 g. of litharge, PbO, contain 3.5862 g. of oxygen, what is the atomic weight of lead?

230. What are the name and formula of a compound of the following composition?

Lead	77.52 per cent.
Carbon	4.49 per cent.
Oxygen	17.98 per cent.

231. How many liters of oxygen are needed to burn 93 g. of phosphorus to P_2O_5? A liter of oxygen = 1.43 grams.

232. 20 g. of phosphorus are burned in a vessel from which nothing is allowed to escape. How many grams will the vessel increase in weight?

233. What volume of air is needed to burn 124 g. of phosphorus to P_2O_5? Assume that air contains 21 per cent by volume of oxygen.

234. If 4 g. of phosphorus when burned yield 9.16 g. of P_2O_5, what is the atomic weight of phosphorus?

235. 2 g. of crystallized copper sulphate, $CuSO_45H_2O$, are dissolved in water, and it is required to precipitate all the copper as CuS. How many grams of iron sulphide and how many grams of hydrochloric acid containing 25 per cent of HCl are needed to generate enough H_2S for the purpose (p. 167)?

236. (*a*) What volume of hydrogen sulphide is produced when 17.6 g. of FeS are dissolved in HCl? (*b*) From how many grams of mercuric chloride dissolved in water will this quantity of H_2S precipitate the mercury as mercuric sulphide (p. 167)?

$$HgCl_2 + H_2S = HgS + 2\,HCl$$

237. What volume of air is needed to burn 500 g. of sulphur to SO_2? Assume that air contains 21 per cent of oxygen by volume.

238. What volume of H_2S escapes when 5 g. of iron sulphide are dissolved in HCl (p. 167)?

239. How many grams of iron sulphide are needed to make 59 liters of H_2S (p. 167)?

240. How many tons of sulphuric acid can be made fron 4 tons of sulphur?

241. How many tons of sulphuric acid can be made from 40 tons of pyrite, FeS_2?

242. The density of sulphuric acid is 1.84. How many grams of sulphur is there in 100 c.c. of it?

243. How many tons of sulphuric acid can be made from 100 tons of pyrite containing 48 per cent. of sulphur?

244. 1.8752 g. of cobalt, when converted into cobalt sulphate, yielded 4.9472 g. What is the atomic weight of cobalt? Assume $S = 32$, $O = 16$. The formula of cobalt sulphate is $CoSO_4$.

245. How many grams of calcium fluoride and how many grams of sulphuric acid containing 96 per cent H_2SO_4 are needed to make 12 g. of pure hydrogen fluoride? See problem 123.

246. How many grams of calcium sulphate and how many grams of hydrofluoric acid are formed when 50 g. of calcium fluoride are heated with sulphuric acid? See problem 123.

247. Manganese dioxide is heated with hydrochloric acid, and the chlorine passed in a solution of potassium iodide. How many grams of iodine will be set free by the chlorine evolved when 12 g. of manganese dioxide are used (p. 221)?

$$2\,KI + Cl_2 \longrightarrow 2KCl + I_2$$

248. Under the same circumstances as in problem 247, how many grams of manganese dioxide are needed to liberate 63.5 g. of iodine?

249. Under the same conditions as in the two preceding problems, how many grams of iodine will be set free when 43.5 g. of manganese dioxide are used?

250. What volume of hydrogen at 13° and 780 m.m. is needed to convert 31.5 g. of Fe_2O_3 into iron?

251. What volume of hydrogen at 14° and 740 m.m. is required to change 20 g. of ferric oxide into iron?

252. If ferric oxide, Fe_2O_3, contains 70 per cent iron and 30 per cent oxygen, what is the atomic weight of iron?

253. If ferrous oxide, FeO, contains 77.8 per cent iron and 22.2 per cent oxygen, what is the atomic weight of iron?

254. The great German chemical works, the Badische Anilin und Soda Fabrik, burns 190,000 T. of coal a year. If the coal contains 70 per cent of carbon, and if there are 310 working days in the year, how many tons of CO_2 escapes daily from the chimneys of the establishment?

255. What volume of carbon dioxide is formed by the burning of 30 l. of carbon monoxide, and what volume of oxygen is required? Solve by inspection.

256. What gas gives rise to the blue flame often seen playing over the surface of a coal fire? How many grams of coal containing 90 per cent of carbon would be needed to make 5,000 l. of this gas at 15° and 750 m.m.?

257. What volume of carbon dioxide must be passed over glowing charcoal to form 42 g. of carbon monoxide?

258. What is the volume (*a*) of 50 g. of carbon monoxide? (*b*) Of 50 g. of carbon dioxide?

259. What volume of carbon dioxide would be produced by burning a diamond weighing 3 g. in oxygen?

260. How many grams of carbon are there in (*a*) 2.8 l. of carbon dioxide; (*b*) 2.8 l. of carbon monoxide?

261. What volume of carbon dioxide at standard conditions is produced by dissolving 25 g. of marble in hydrochloric acid? See problem 138.

262. What volume of carbon dioxide at 12° and 750 m.m. is produced by dissolving 35 g. of marble in hydrochloric acid? See problem 138.

263. What is the weight of 38 l. of methane at 31°?

264. What is the weight of 10 l. of acetylene?

265. How many grams of calcium carbide is needed to produce 5.6 l. of acetylene? See problem 270, 1st equation.

266. A town is to be lighted with acetylene. It is calculated that the consumption of the gas will be 70,000 l. per day. How many metric

tons of calcium carbide will be required per month of thirtv days? See problem 270, 1st equation.

267. How many grams of carbon are there in 32 l. of acetylene?

268. How many grams of sodium acetate are needed to make 8 l. of methane?

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3$$

269. How many liters of oxygen at 10° and 780 m.m. are needed to burn completely the methane obtained when 41 g. of sodium acetate are heated with sodium hydroxide?

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3$$
$$CH_4 + 20_2 = CO_2 + 2\,H_2O$$

270. Calcium carbide is treated with water and the acetylene burned. 28 l. of carbon dioxide at 15° and 740 m.m. resulted from the combustion. How many grams of calcium carbide were taken, and what volume of oxygen at 15° and 740 m.m. was needed to burn the acetylene?

$$CaC_2 + 2\,H_2O = Ca(OH)_2 + C_2H_2$$
$$C_2H_2 + 50 = 2\,CO_2 + H_2O$$

APPENDIX

I—THE METRIC SYSTEM

Length

1 inch = 2.54 centimeters. 1 centimeter = 0.3937 inch. For practical purposes it is useful to remember that 1 inch = about $2\frac{1}{2}$ cm.

Volume

1 liter = 1000 cubic centimeters
1 liter = 0.2642 gallon
1 liter = 1.057 quarts
1 pint = 0.473 liter
1 quart = 0.946 liter
1 fluid ounce = 29.57 cubic centimeters
1 fluid dram = 3.7 cubic centimeters

For practical purposes it is useful to remember that 1 fluid ounce = about 30 cubic centimeters. The *drop* is not a scientific unit. Its volume depends upon the orifice and the speed of dropping, as well as upon the nature of the liquid.

The *small* test tubes used in the laboratory average about 15 cm. in length by 1.8 cm. in diameter. Their average capacity is rather less than 40 cubic centimeters. It is convenient to use them in rough measurements of volumes of liquids.

Weight

The gram is the weight of 1 cubic centimeter of water at 4°.

1 gram = 0.035 ounce (avoirdupois)
1 gram = 15.43 grains
1 ounce (avoirdupois) = 28.35 grams
1 kilogram = 1000 grams
1 kilogram = 2.2 pounds (avoirdupois)
1 metric ton = 1000 kilograms
1 metric ton = 2205 pounds (avoirdupois)

It will greatly improve the quality of the student's laboratory work if he will endeavor to form a fairly accurate idea of the quantity denoted by a gram. To assist in this, the weights of some common coins are given in grams. The weights are only roughly approximate.

cent	3.1	grams
nickel	5	"
dime	2.5	"
quarter	6.5	"
half-dollar	13.3	"
silver dollar	26.6	"

II—THE CENTIGRADE SCALE OF THE THERMOMETER

Formulæ for converting Fahrenheit degrees into Centigrade, and the reverse.

$$F^\circ = \tfrac{9}{5}\ (C^\circ + 32)$$
$$C^\circ = \tfrac{5}{9}\ (F^\circ - 32)$$

The Conversion Table on the opposite page is due to Dr. Leonard Waldo. The principle is the same as that of a table of logarithms. Thus:

(1) What is the Fahrenheit equivalent of 1347°C?

Pass down the left-hand column to 1300°C. In the same horizontal line in the 6th column to the right we find that the Fahrenheit equivalent of 1340°C is 2444°F. In the *upper* part of the right-hand margin we find that the remaining 7°C = 12°.6F. Hence,

$$1347^\circ C = 2444^\circ F + 12^\circ.6F = 2456^\circ.6F$$

(2) What is the Centigrade equivalent of 3367°F?

The nearest temperature to 3367°F in the table is 3362°F, which corresponds to 1850°C. In the lower part of the right-hand margin we find that 5°F = 2°.78C. Hence,

$$3367^\circ F = 1850^\circ C + 2^\circ.78C = 1852^\circ.78C$$

Centigrade-Fahrenheit Conversion Table

C°	0	10	20	30	40	50	60	70	80	90
	F	F	F	F	F	F	F	F	F	F
−200	−328	−346	−364	−382	−400	−418	−436	−454		
−100	−148	−166	−184	−202	−220	−238	−256	−274	−292	−310
−0	+32	+14	−4	−22	−40	−58	−76	−94	−112	−130
0	32	50	68	86	104	122	140	158	176	194
100	212	230	248	266	284	302	320	338	356	374
200	392	410	428	446	464	482	500	518	536	554
300	572	590	608	626	644	662	680	698	716	734
400	752	770	788	806	824	842	860	878	896	914
500	932	950	968	986	1004	1022	1040	1058	1076	1094
600	1112	1130	1148	1166	1184	1202	1220	1238	1256	1274
700	1292	1310	1328	1346	1364	1382	1400	1418	1436	1454
800	1472	1490	1508	1526	1544	1562	1580	1598	1616	1634
900	1652	1670	1688	1706	1724	1742	1760	1778	1796	1814
1000	1832	1850	1868	1886	1904	1922	1940	1958	1976	1994
1100	2012	2030	2048	2066	2084	2102	2120	2138	2156	2174
1200	2192	2210	2228	2246	2264	2282	2300	2318	2336	2354
1300	2372	2390	2408	2426	2444	2462	2480	2498	2516	2534
1400	2552	2570	2588	2606	2624	2642	2660	2678	2696	2714
1500	2732	2750	2768	2786	2804	2822	2840	2858	2876	2894
1600	2912	2930	2948	2966	2984	3002	3020	3038	3056	3074
1700	3092	3110	3128	3146	3164	3182	3200	3218	3236	3254
1800	3272	3290	3308	3326	3344	3362	3380	3398	3416	3434
1900	3452	3470	3488	3506	3524	3542	3560	3578	3596	3614
2000	3632	3650	3668	3686	3704	3722	3740	3758	3776	3794
2100	3812	3830	3848	3866	3884	3902	3920	3938	3956	3974
2200	3992	4010	4028	4046	4064	4082	4100	4118	4136	4154
2300	4172	4190	4208	4226	4244	4262	4280	4298	4316	4334
2400	4352	4370	4388	4406	4424	4442	4460	4478	4496	4514
2500	4532	4550	4568	4586	4604	4622	4640	4658	4676	4694
2600	4712	4730	4748	4766	4784	4802	4820	4838	4856	4874
2700	4892	4910	4928	4946	4964	4982	5000	5018	5036	5054
2800	5072	5090	5108	5126	5144	5162	5180	5198	5216	5234
2900	5252	5270	5288	5306	5324	5342	5360	5378	5396	5414
3000	5432	5450	5468	5486	5504	5522	5540	5558	5576	5594
3100	5612	5630	5648	5666	5684	5702	5720	5738	5756	5774
3200	5792	5810	5828	5846	5864	5882	5900	5918	5936	5954
3300	5972	5990	6008	6026	6044	6062	6080	6098	6116	6134
3400	6152	6170	6188	6206	6224	6242	6260	6278	6296	6314
3500	6332	6350	6368	6386	6404	6422	6440	6458	6476	6494
3600	6512	6530	6548	6566	6584	6602	6620	6638	6656	6674
3700	6692	6710	6728	6746	6764	6782	6800	6818	6836	6854
3800	6872	6890	6908	6926	6944	6962	6980	6998	7016	7034
3900	7052	7070	7088	7106	7124	7142	7160	7178	7196	7214
C°	0	10	20	30	40	50	60	70	80	90

C°	F°
1	1.8
2	3.6
3	5.4
4	7.2
5	9.0
6	10.8
7	12.6
8	14.4
9	16.2
10	18.0

F°	C°
1	56
2	1.11
3	1.67
4	2.22
5	2.78
6	3.33
7	3.89
8	4.44
9	5.00
10	5.56
11	6.11
12	6.67
13	7.22
14	7.78
15	8.33
16	8.89
17	9.44
18	10.00

EXAMPLES: 1347°C = 2444°F + 12°.6F = 2456°.6F: 3367°F = 1850°C + 2°.78C = 1852°.78C

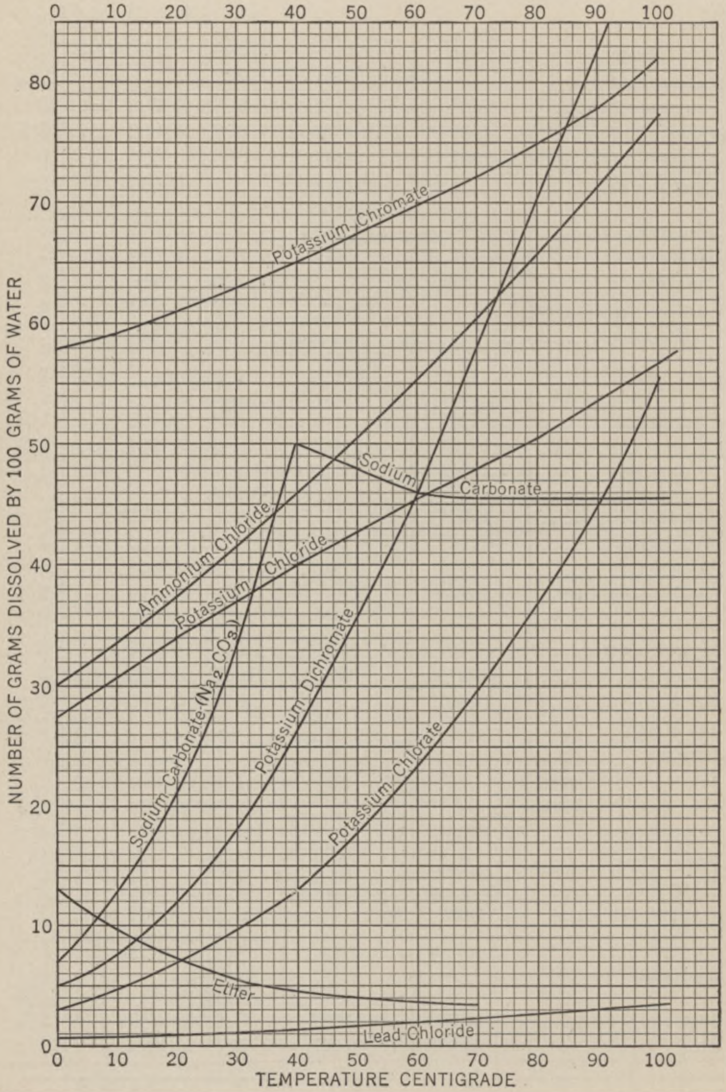
Some Important Temperatures

Centigrade.	Fahrenheit	
−273°	−459°.4	Absolute zero
−268°.5		Helium boils
−256°		Hydrogen freezes Boiling-points are given for 760 mm. pressure.
−253°		Hydrogen boils
−214°		Nitrogen freezes
−194°		Nitrogen boils
−130°		Alcohol freezes (ethyl)
− 39°.5	−39°.1	Mercury freezes
0°	32°	Ice melts
10°.5		Sulphuric acid freezes
37°		Average temp. of human body
60°		Wood's fusible metal melts
78°.5		Alcohol boils (ethyl)
10°	212°	Water boils (760 mm. pressure)
114°.5		α-Sulphur melts
120°		β-Sulphur melts
160°		Sugar (sucrose) melts
232		Tin melts
320		Cadmium melts
327°		Lead melts
419°		Zinc melts
448°		Sulphur boils
525°	977°	First visible red heat
660°		Aluminium melts
700°	1292°	Dull red heat
772°		Table-salt melts
1000°	1832°	Bright red heat
1064°		Gold melts
1100°		Copper melts
1200°	2192°	Bright orange heat
1375°		Temp. of glass-furnace
1500°	2732°	Bright white heat. Temp. of open-hearth furnace
2000°	3632°	Temp. of Welsbach mantle
4000°	7232°	Temp. of electric arc
6000°	10,832°	Temp. of sun

III—NUMERICAL DATA FOR SOME OF THE MORE IMPORTANT ELEMENTS.

Name.	*Melting-Point.*	*Boiling-Point.*	*Specific Gravity.*	*Specific Heat.*	*Molecular Formula.*	*Valence.*
Aluminium......	660°	....	2.58	0.22	....	3
Antimony.......	430°	White heat	6.7	0.052	....	3;5
Argon..........	−190°	−185°	....	......	Ar	0
Arsenic.........	....	450° (sublimes)	5.7	0.083	As_4	3;5
Bismuth.........	270°	1100°?	9.9	0.031	....	3
Bromine........	−7°.3	63°	3.2	0.084	Br_2	1
Calcium.........	760°	....	1.6	0.18	....	2
Carbon (graphite)	....	3600°	2.2	0.454	....	4
(Diamond).....	....	.... (sublimes)	3.5	0.45	....	...
Chlorine........	−102°	−33°.5	1.33 (liquid)	......	Cl_2	1
Chromium.......	1515°	....	6.8	0.100	....	3;6
Copper..........	1100°	2100°	8.9	0.094	....	1;2
Fluorine........	−223°	−187°	1 (liquid)	......	F_2	1
Gold............	1064°	....	19.5	0.0316	....	3
Hydrogen.......	−257°	−253°	....	......	H_2	1
Iodine..........	114°	184°	4.95	0.054	I_2	1
Iron (wrought).	1600°	....	7.5	0.112	....	2;3
Lead............	327°	1500°	11.3	0.031	....	2
Magnesium......	750°	1100°	1.75	0.245	....	2
Mercury........	−39°.4	357°	13.6	0.032	Hg	2
Nickel..........	1450°	....	8.8	0.109	....	2
Nitrogen........	−214°	−194°	....	......	N_2	3;5
Oxygen.........	....	−181°	....	......	O_2	2
Phosphorus { White	44°	290°	1.83	0.202	....	....
Phosphorus { Red	....	....	2.16	0.17	P_4	3;5
Platinum........	1775°	....	21.5	0.04	....	4
Potassium.......	62°.5	720°	0.86	0.165	K	1
Silicon..........	White heat	Under 3500°	2.5	0.181	....	4
Silver..........	960°	White heat	10.47	0.057	....	1
Sodium..........	95°.6	742°	0.97	0.29	Na	1
Sulphur.... { α	114°.5	448°	2.07	......	....	....
Sulphur.... { β	120°	448°	1.95	0.18	S_8	2;4;6
Tin.............	232°	1600°	7.3	0.0562	....	2;4
Zinc............	419°	930°	7	0.096	....	2

IV—SOLUBILITY CURVES FOR SOME IMPORTANT SUBSTANCES



V

Logarithms.

Proportional parts

Nat. Number	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

Logarithms.

Proportional parts

Nat. Number	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9335	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

VI—ABUNDANCE OF THE ELEMENTS IN NATURE

List of the Elements in Order of Abundance.	Composition of the solid crust of the earth.	Composition of sea-water	Composition of the earth's crust, including the ocean and the atmosphere.
	Per cent.	Per cent.	Per cent.
Oxygen	47.29	85.79	49.98
Silicon	27.21	....	25.30
Aluminium	7.81	....	7.26
Iron	5.46	....	5.08
Calcium	3.77	0.05	3.51
Magnesium	2.68	0.14	2.50
Sodium	2.36	1.14	2.28
Potassium	2.40	0.04	2.23
Hydrogen	0.20	10.67	0.94
Titanium	0.33	....	0.30
Carbon	0.22	....	0.21
Chlorine	0.01	2.08	0.15
Phosphorus	0.10	....	0.09
Manganese	0.08	....	0.07
Sulphur	0.03	0.09	0.04
Barium	0.03	....	0.03
Nitrogen	0.01	....	0.02
Chromium	0.01	....	0.01
	100 per ct.	100 per ct.	100 per ct.

The crust of the earth does not contain as much as 0.01 per cent. of any of the remaining 60 elements. The entire 60 make up but a small fraction of 1 per cent.

The student should notice the striking *inequality* in the distribution of the elements. Two of them, oxygen and silicon, make up three-quarters of the earth's crust. *Native* elements play only an unimportant part in the construction of the planet.

The sun and the stars, comets, and meteors are composed of the same elements which we find upon the earth. A sample of magnesium, obtained from a meteor composed of magnesium silicate, proved to have the same *atomic weight* as the magnesium found upon the earth.

INDEX

The topics in bold-faced type are those required by the syllabus of the College Entrance Examination Board. As a rule, a subject which occurs several times, under different headings, is printed in bold-faced type once only.

TABLE OF ATOMIC WEIGHTS

NAME.	Symbols.	Exact Values.	Approximate Values.	NAME.	Symbols.	Exact Values.	Approximate Values.
Aluminium	Al	27.1	27	Neodymium	Nd	143.6	......
Antimony	Sb	120.2	120	Neon	Ne	19.94	......
Argon	A	39.92	......	*Nickel*	Ni	58.70	58.7
Arsenic	As	75.0	75	*Nitrogen*	N	14.01	14
Barium	Ba	137.43	137	Osmium	Os	190.8	......
Beryllium	Be	9.1	......	**Oxygen**	**O**	**16.000**	**16**
Bismuth	Bi	208.0	208	Palladium	Pd	106.5	......
Boron	B	11.0	11	*Phosphorus*	P	31.0	31
Bromine	Br	79.955	80	*Platinum*	Pt	195.2	195
Cadmium	Cd	112.4	112	*Potassium*	K	39.14	39
Cæsium	Cs	132.9	......	Praseodymium	Pr	140.5	......
Calcium	Ca	40.1	40	*Radium*	Ra	226.	......
Carbon	C	12.00	12	Rhodium	Rh	103.0	......
Cerium	Ce	140.0	......	Rubidium	Rb	85.44	......
Chlorine	Cl	35.455	35.5	Ruthenium	Ru	101.7	......
Chromium	Cr	52.14	52	Samarium	Sa	150.0	......
Cobalt	Co	59.00	59	Scandium	Sc	44.0	......
Columbium	Cb	94.0	......	Selenium	Se	79.2	......
Copper	Cu	63.60	63.5	*Silicon*	Si	28.4	28.5
Erbium	Er	166.0	......	*Silver*	Ag	107.93	108
Fluorine	F	19.0	19	*Sodium*	Na	23.05	23
Gadolinium	Gd	156.?	......	Strontium	Sr	87.68	87.5
Gallium	Ga	70.0	......	*Sulphur*	S	32.065	32
Germanium	Ge	72.5	......	Tantalum	Ta	181.0	......
Gold	Au	197.2	197	Tellurium	Te	127.5?	......
Helium	He	4.0	......	Terbium	Tb	160.0	......
Hydrogen	H	1.0075	1	Thallium	Tl	204.15	......
Indium	In	115.0	......	Thorium	Th	233.0	......
Iodine	I	126.97	127	Thulium	Tu	171.0?	......
Iridium	Ir	193.0	......	*Tin*	Sn	119.0	119
Iron	Fe	55.9	56	Titanium	Ti	48.17	......
Krypton	Kr	81.8	......	*Tungsten*	W	184.0	......
Lanthanum	La	138.9	......	Uranium	U	238.5	239
Lead	Pb	206.92	207	Vanadium	V	51.2	......
Lithium	Li	7.03	......	Xenon	X	128.0	......
Magnesium	Mg	24.32	24	Ytterbium	Yb	173.0	......
Manganese	Mn	55.02	55	Yttrium	Y	89.0	......
Mercury	Hg	200.0	200	*Zinc*	Zn	65.40	65.5
Molybdenum	Mo	96.0	......	Zirconium	Zr	90.6	......

The more important elements are in italics. The *approximate values* should be used in solving problems.