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PREFACE

The emphasis on the teaching of science in the schools, together with the attention given to it by newspaper, magazine, radio, and television, brings many young people to college with a fair acquaintance with the terminology and main generalizations of chemistry. The college course in chemistry must then seek to broaden and deepen the student's knowledge of the quality of scientific facts, to outline the precise and quantitative nature of scientific evidence, and to emphasize the rigor of scientific thinking. A memory of these features of the discipline may well be the most important residue that the average young student carries with him from his college course in chemistry. This book is an attempt to provide this insight into the nature of science as embodied in the language and framework of chemistry.

The authors have sought to emphasize the fundamental methods of science in arriving at truth, and to make the theoretical structure of the science of chemistry stand out with clarity and simplicity. We have adhered to the sound pedagogical practice of the original McPherson and Henderson texts in presenting a full measure of descriptive chemistry, together with a considerable body of experimental fact in the first part of the book, to serve as a basis for deriving the periodic law, the theory of atomic structure, and other theories. Chapters on oxygen, hydrogen, and the atmosphere are introduced early to provide, also, some background material for stimulating laboratory work and to give the student, as soon as possible, some feeling for the characteristic properties and behavior of chemical substances. Considerable attention has been given to industrial processes, for the authors believe that the science loses much in interest if free reference to its applications in the industries is omitted, and that much enjoyment lies in the development of a confident knowledge of how things are made.

The major changes in the present revision include the following: Four of the introductory chapters have been rewritten; the treatment of atomic and molecular weights has been simplified and shortened; the chapter on nuclear energy, formerly placed at the end of the book, has been revised and brought forward and integrated with the other two chapters on atomic structure. The chapters on carbon and silicon have been combined, to show the striking resemblances and differences in behavior of these two elements. A new chapter, which discusses explosives, jets, and rockets, has been added; and our compact set of chapters on organic

chemistry has been reduced about a third. The final chapter presents a story of fuels and power, past and present, with a brief account of nuclear energy and solar energy reaching into the future.

Our text is not written alone for the student who expects to major in chemistry. It is written for all comers: for the students who are seeking a liberal education, and for those who plan to become teachers; for those who are interested in engineering or in agriculture; for those who are preparing for medicine, or planning a career in a related profession or science. Its prime purpose is to provide a systematic account of the principles of general chemistry.

Although the book carries our four names, it is in no sense the work of ourselves alone. It is a pleasure to acknowledge the help of present colleagues and of former students, and our great indebtedness to Dr. William McPherson and Dr. William E. Henderson, whose earlier texts were the inspiration for this one.

The Authors

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TEXTBOOK OF CHEMISTRY



AMEDEO AVOGADRO

(1776–1856)

Professor at the University of Turin, Italy

Renowned for formulating the fundamental law of modern chemistry known as Avogadro's law

From a photograph of a statue erected to his memory at Turin

CHAPTER 1

INTRODUCTION

The Adventure of Science and the Scientific Method

In Walpole's famous story, *The Three Princes of Serendip*, it is told how the three princes set out on adventurous travels to see the world. They had been well educated, and they had the gift of being able to find valuable and agreeable things unexpectedly. We may let these princes point the way to our own story, since they would have made apt students of science: (1) They were seeking adventure; and (2) they were exceptionally thoughtful observers.

1. **Science the great modern adventure.** When someone speaks of the days of adventure, the mind turns to the travels of Marco Polo, the voyages of Columbus or Magellan or Drake, the overland trail of Lewis and Clark or of Livingstone, the polar quests of Peary or Scott or Byrd.

But there are adventures other than geographical ones, other unknown regions to explore besides those of new continents or ocean islands; and of these the fields of science are among the most fascinating. In the domains of science are continual quests in search of an understanding of the world in which we live, and these quests are adventures just as alluring and just as daring as those that led the great explorers into the remote places of the world. And what leads the man of science into his adventure? It is his great *curiosity* to know more about some of the facts of nature that neither he nor anyone else understands at the present time. He is a true adventurer into the unknown.

In addition, he has a second motive. He knows that the discovery of new facts, a better understanding of the nature of the material world, the production of new materials from the crude ones found in nature, the increasing comprehension of the mechanics and chemistry of living organisms, all contribute, when properly used, to more comfortable and healthful human living.

The young scientist prepares for his adventure like any other wise explorer. Those early captains got the best ships they could command, manned them with hardy sailors, provisioned them with abundant stores both of food and of repair supplies, and looked to their means of defense and (in later years) to a supply of lime juice to ward off scurvy. The

adventuring scientist must equip himself with all the available information about the region in which his quest is to lie; and he must patiently acquire skill in experimentation, just as the sea captain must master the navigation of his ship. The science courses of schools and colleges, the libraries they support, the laboratory exercises they require, together with a discipline in clear thinking, constitute the equipment for the adventure that lies before the young scientist.

2. Observation and experiment. Many advances in science have come through workers with the ability, like that of the three princes of Serendip, to catch the significance of a chance observation that would escape recognition by ordinary observers. In such a way Professor Becquerel discovered radioactivity, and William Perkin, an eighteen-year-old schoolboy, made the first aniline dye.

But the advance of science is not very largely dependent upon fortunate or unexpected happenings. A scientist proceeds on his quest systematically; he gathers facts about the various phenomena of nature, both by observing and by experimenting. He formulates laws from the facts, and constructs theories to explain the facts and laws. In making observations he usually looks at nature as he finds her. But in his experiments he poses his questions to nature under conditions of his own contriving. It is mainly through experiment that the insight we have obtained into the nature of the material world has come.

The Science of Chemistry · Chemistry is the science of the structure of matter and of the transformations which material things undergo. It is one of the natural sciences, as are also astronomy, physics, geology, and the biological sciences. Chemistry is intimately related to the other sciences, and underlies most of them. The student or adventurer in physiology or any of the biological sciences, in geology, in astronomy, in the problems of agriculture and of industry, finally comes to the point where he must follow a chemical trail if he is to go farther in his adventure.

Science and the Arts and Crafts · Science is young; the arts and crafts are very old. In the arts and crafts one strives for results and excellencies; in science one strives for understanding.

From the time people began to live together in communities, various arts and crafts slowly developed to keep pace with the needs of community life. The smelting of iron and other metals required a knowledge of fluxes, and the colored, glasslike slags which were by-products of the smelting process came to be used as enamels for coating earthenware tiles. It was not long before people learned to fashion the easily fusible slags into hollow glass vessels and flat plates, although transparent glass came much later. Dyes, pigments, mortars, cements, soaps, and many

other chemical substances were prepared and used by the ancient peoples.

The excellence attained in these skills through centuries of time might lead one to the conclusion that long ago a real beginning had been made in the science of chemistry. But this would be a mistake. The interest in them was entirely practical, and the reasons for the changes produced were neither understood nor sought for.

Greek Thinkers · It must not be supposed that no one among the ancient peoples was curious. The Greek thinkers (philosophers) had many ideas as to how material things were made up. Some of them, in fact, thought that all things are really composed of great numbers of small bodies called *atoms*, and this we now know to be true. But their thinking failed to make contact with *facts* obtained by *experimentation*; they arrived, therefore, at wrong conclusions which, asserted authoritatively in the writings of Aristotle, persisted for centuries, until, and even after, the results of experiment showed them to be wrong.

The Middle Ages · Experimentation began to be carried out extensively during the Middle Ages by the *alchemists*, who bent their efforts to "purifying" the baser metals or transmuting them into gold. Their efforts all failed, and, as hope dimmed, some of them turned to other efforts. The human body for the first time came to be regarded as being made up of the same materials that constitute other objects about us. Illness was thought to be due to some definite lack or excess of some body constituent, and the real object of alchemy was proclaimed to be *iatrochemistry*, the preparation of medicines wherewith to repair the deficient body.

Two New Chemical Problems · Early in the eighteenth century two new problems absorbed the interest of chemical workers, now chiefly pharmacists, university professors, and private enthusiasts. (1) What happens when wood or a candle or a metal burns? (2) What is a gas, and are there varieties of gases? Until these questions were answered chemistry could have no real foundation.

The Phlogiston Theory of Combustion · The effort to explain combustion resulted in what became known as the phlogiston theory. This theory assumed that every burnable thing consists of a calx, or ash, together with a quantity of a mysterious, airlike principle called *phlogiston*, and that the act of burning is the escape of this phlogiston from the combustible substance. For about seventy-five years this theory ruled the minds of chemical workers, but experiment steadily tended to show that it could not be true and that a better explanation must be found.

The Discovery of Oxygen · Until about the time of the American War of Independence the idea of a gas was a very vague one in the minds of

chemists. They called gases "airs." Many believed that all these airs were much alike. Then Joseph Priestley in England devised a method for collecting different airs from various sources over mercury (in which they were not soluble) and noted their properties. He obtained the airs by heating various materials, and was able to show that about ten airs had each its own characteristics and were distinctly different things. In particular he isolated pure oxygen and showed how brilliantly a combustible substance burns in this air, or gas.

The Nature of Burning · At about the same time the great French chemist Lavoisier was making many experiments which were characterized by the careful *weighing* of all materials that took part in a given chemical change and that resulted from it. He had made many such experiments on combustion, and was sure that there is some one thing in the air that makes burning possible. With the discovery of oxygen, he quickly proved that combustion is the chemical action between the oxygen of the air and the combustible material.

Lavoisier's emphasis on the quantities of substances involved in chemical changes set the pattern for the scientific approach or the scientific method on which chemistry as a science is based: a *curiosity* about why things happen, and a *test of all conclusions* by a comparison with the results of quantitative experiments.

The Scientific Method · In satisfying their curiosity and testing their conclusions, scientists have discovered a method for discovering. The essential features of this *scientific method,* as we have already hinted, are the following:

1. **Get the facts.** The chemist must have a knowledge of all known facts that have to do with his field of work, for facts are the basis of all sciences.

2. **Formulate and use laws.** The meaning of a law in science may be made clear by an example. About the middle of the seventeenth century Robert Boyle became interested in the extent to which a measured volume of air is changed by a change in pressure. By careful experiment he found that if he doubled the pressure, the volume decreased to one half its former value; if he diminished the pressure by one half, the volume doubled. So he concluded that, for a given quantity of air, the volume was inversely proportional to the pressure. This was a *fact* about a property of air. It was reasonable to go beyond this single fact, however, and make the *hypothesis* that all gases behave like air in this respect. When, later, other gases had been discovered, and were found to follow the same rule, this hypothesis was verified, and it thus proved to be a statement of a general physical relationship between volume and pressure,

now called Boyle's *law*. A law is therefore a generalization, based on the results of experiments, which is found to apply to all cases where similar experiments are carried out.

3. **Propose theories.** As scientists, working with gases, became more and more familiar with the properties of gases, they found that Boyle's law was only one of several general laws which described gaseous behavior. The next step was to go behind the laws and find some general unifying principles which would explain why all gases obeyed the same laws; in other words, the next step was to imagine what could be common to the make-up of all gases which causes them to behave in the same way. When such general, unifying principles were found, they were arranged in an orderly fashion and proposed as a *theory* to explain the properties of gases as recorded in the laws describing their behavior. The theory proposed was that all gases, of whatever sort, were made up of billions and billions of tiny particles which were in ceaseless motion; and it was found that this proposal explained satisfactorily the known behavior of gases. No one had ever seen these particles; they could only be imagined to be present. A theory, then, is a happy imaginative guess beyond present knowledge, which explains the laws based upon the experimental facts.

4. **Test and use the theories.** It is not sufficient to propose a theory; it must also be tested and shown to be correct by as many ingenious experiments as possible. If, as the theory above proposes, there are moving particles in gases, calculable effects will appear when the flow of gases through tubes and the conduction of heat through gases are studied. Experiments are then set up to examine the flow and conduction phenomena to see whether or not the predictions of the theory are correct. If the theory passes these experimental tests, then scientists accept it as being true; if it fails to pass these tests, it is discarded, and a new theory is proposed for further test. Thus the phlogiston theory was discarded and replaced.

A successful or plausible theory may be used to extend our knowledge, since out of a theory will come predictions of new effects and the raising of new questions. As the answers and the experimental facts needed to check the predictions are found, new facts accumulate. Then new theories or modified theories are developed to explain them. So our body of knowledge grows, facts and theories coming along together.

The Modern Chemist · With such a tool as the scientific method, the chemist has at his disposal a procedure for inventing new processes and preparing new materials suited to the needs of modern society. Experiment, experiment, and experiment have expanded the basic body of facts

available to the chemist; laws relating to the behavior of matter have been formulated, and theories proposed and tested. The chemist, now far more advanced than was Lavoisier in a fundamental understanding of the nature of combustion, has designed new and efficient fuels for automobile and airplane engines, and superfuels to launch and drive jet planes and rockets. He has produced new textile fibers, new building materials, new dyes, new weapons, and new medicines. Chemistry has indeed become a great adventure, with enchanting lands beckoning in every direction, and vast expanses of yet unexplored territory stretching to the horizon.

It is upon this adventure that we now embark. We must learn what is already known and how to apply the methods of the chemist to the investigation of the world which lies beyond. A beginning in this direction will be found in the following pages.

CHAPTER 2

MATTER AND ENERGY

Of what stuff is our world made? Is it made of different forms and kinds of many unrelated substances? Or is it made of only one kind of stuff that appears in many different forms? Such questions aroused the curiosity of the early philosophers. Empedocles in 450 B.C. proposed the theory that the universe is made of four things: fire, air, earth, and water. He assumed that the different materials of the universe are made up of combinations of these four in different proportions, but that each is eternal. This theory, modified by Plato and Aristotle, persisted until the seventeenth century A.D.

Today, we interpret our physical world in terms of *matter* and *energy*, each of which can exist in a variety of forms. As we watch the changes that occur in the things about us, the corrosion of metals, the weathering of rocks, the growth of flowers, the burning of coal, we note that there are two things involved in all of them—the *matter* that undergoes the change, and the *energy* that causes the change or results from it.

We can focus our study and attention on these two great entities—matter and energy. We shall study the *properties, composition, and structure of matter, the changes which it undergoes, and the accompanying energy changes.* This is the science of chemistry.

Matter

Matter has been defined as *anything which occupies space and possesses mass*; and the mass or actual "stuff" of a piece of matter may be measured (1) by the *weight*, or (2) by the *inertia* of the matter.

1. **Weight.** Every piece of matter on the earth is attracted downward by gravity; and the force of this gravitational attraction is called the weight of the piece of matter. The weight is proportional to the mass, and for the practical purposes of the chemist the two terms *mass* and *weight* may be used interchangeably.

The instrument for measuring weight (or mass) is the chemical balance (Fig. 2-2). With such a balance a given sample of matter, on the left-hand pan, is "balanced" against standard weights on the right-hand pan.

2. **Inertia.** We know that every material body possesses inertia. By this we mean that if the body is at rest, force will be required to set it in

motion; and if it is in motion, a force will be required to stop it. We can measure this force in any given case, and so measure the inertia of the body. The mass of a body is that property that gives it inertia. The larger the mass of a body—and so the greater its inertia the smaller will be the effect of a given force upon it (Fig. 2-1).

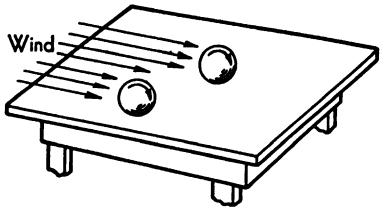


Fig. 2-1. Effect of Inertia · If two balls of equal size but of different masses are blown along a table top by a wind acting with equal force on each, the ball of smaller mass, and smaller inertia, will be blown ahead of the heavier ball

Conservation of Mass · Since the outward form of matter is constantly changing, it would perhaps seem possible that its mass is also undergoing variation. The mass of a lump of coal is certainly much greater than that of the ashes which result from its burning. If, however, we collect the gases formed and take into account all the materials involved in the burning, we find that the total mass remains unchanged. All our experience goes to show that this is true, and that *in all ordinary changes in matter the total mass is neither increased nor decreased.* This generalization is known as the *law of conservation of mass* (Fig. 2-2). We shall see later that under some conditions the mass does change, as in nuclear reactions.

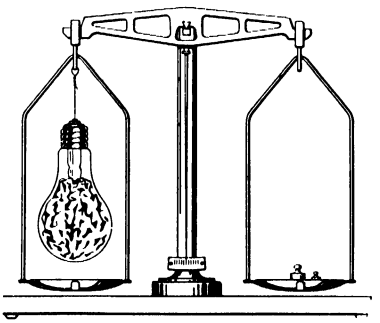


Fig. 2-2. A Photoflash Bulb · The bulb contains aluminum foil and oxygen gas By connecting the bulb to a battery, the aluminum foil is heated and combines with the oxygen, with a brilliant flash of light. Experiments show that the weight of the bulb before the flash and the weight after are the same

Substances · There are many *kinds* of matter; iron is a *kind* of matter, as are wood, glass, gold, alcohol, etc. These different kinds of matter we call *substances.*

The Properties of Substances · By the term *properties* we mean all those marks or characteristics by which a given substance is identified. More than a hundred measurable properties are known. Many of these are easily measurable, such as *density, temperature of melting, temperature of boiling,* and *solubility.* Others are not so easily measured: *color, hardness, luster, viscosity.*

Effect of Physical Conditions on Properties of Substances · Many of the properties of substances depend upon the physical conditions under which they are observed, especially on the temperature and pressure. For example, the boiling point of water decreases as the atmospheric pressure decreases; hence water boils at a lower temperature on a moun-

tain top than at the base of the mountain. The density of most liquids decreases as the temperature increases. Most substances are more soluble in hot water than in cold water.

Physical and Chemical Changes · Among the properties of a substance is its ability to undergo certain changes in form and state which do not alter the fundamental nature of the substance. Thus a piece of metal may be drawn out into a wire, or a rock may be broken up into small pieces. The metal is still metal and the rock is still rock. Such changes are called *physical changes.* Even the change of a substance from solid to liquid, as in the melting of ice, is generally considered to be a physical change.

We shall find later (p. 22) that substances undergo more deep-seated changes under suitable conditions. For example, mercuric oxide is decomposed into mercury and oxygen gas when heated to a high temperature. Such a change is called a *chemical change.* We recognize the fact that a chemical change has taken place by the disappearance of one or more substances and the appearance of one or more new substances, the properties of which are different. The tendencies of a substance to undergo or to resist chemical change are called the *chemical properties* of the substance.

Nuclear Changes · We shall find later that matter may undergo a third type of change, even more profound than the physical and chemical changes just described, a kind of change which involves the very nature of matter itself, and includes such changes as occur in the disintegration of radium, the explosion of an atomic bomb, and even the changes which produce the energy in the sun. Such changes are called *nuclear changes.* We shall postpone discussion of such changes until a later time.

Units of Measurement · From earliest times man has used certain convenient standards for measurement. For example, the length of a man's foot was taken as the standard of length or distance, and the distance between two points was measured by finding out how many times a foot could be placed between them. Human feet vary in size, however, so that the official measuring foot in one locality would be different from that in another. Similar confusion of standards existed in the measurement of the other quantities, such as volume and weight. To end this confusion the National Assembly of France in 1791 instructed the French National Academy of Science to appoint a committee to make recommendations for a system of uniform standards. The system of units that was devised, which serves as the basis for the system used in most European countries today, and in all scientific work, is known as the centimeter-gram-second (cgs) system. This system, which includes within itself the metric system, has the advantage that the common units (except

for the time units) are related by tens or decimals, differing in that respect from the English, or foot-pound-second (fps), system, with its 12 inches to the foot, 3 feet to the yard, 16 ounces to the pound, etc.

Units of Time, Length, Area, Volume, and Mass (Weight) · The *second*, the unit of time, is defined as 1/86,400th part of a mean solar day; 60 (seconds) × 60 (minutes) × 24 (hours) = 86,400 seconds per day.

On this page is shown the actual size of the metric system of units of length, area, volume, and mass (weight), so that we may carry in mind what the magnitudes are. In the Appendix, tables give some of the commonly used centimeter-gram-second units and their equivalents in the English system.

The *centimeter* (cm), unit of length, is $\frac{1}{100}$ of a meter, which is the distance arbitrarily chosen as a standard of length. It is the distance between two marks scratched on a bar of platinum-iridium kept at constant temperature at the International Bureau of Weights and Measures at Sèvres, near Paris. The relationship of a centimeter to an inch (in.) is shown in Fig. 2-3. A square centimeter (cm^2) and a square millimeter (mm^2) are shown in Fig. 2-4, and a cubic centimeter (cc) and a cubic millimeter (mm^3) in Fig. 2-5.

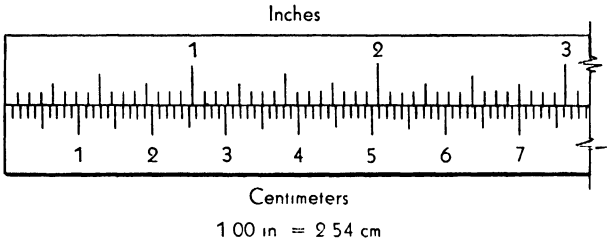


Fig. 2-3. The Centimeter and the Inch Compared

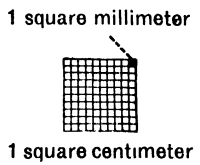


Fig. 2-4. Units of Area

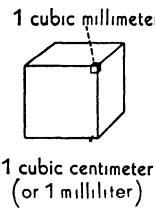


Fig. 2-5. Units of Volume



Fig. 2-6. Unit of Mass (Weight)

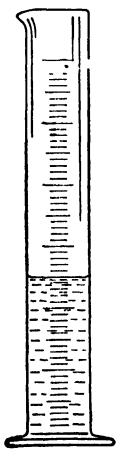


Fig. 2-7. A Cylinder Graduated in Cubic Centimeters or Milliliters. Used for Measuring the Volume of Liquids

The gram (g), unit of mass (weight), is $\frac{1}{1000}$ of the mass of a piece of metal (platinum-iridium) called the standard kilogram, and also kept at the International Bureau at Sèvres. The National Bureau of Standards

in Washington possesses an accurate replica of this standard, and of the standard meter (Fig. 2-8).

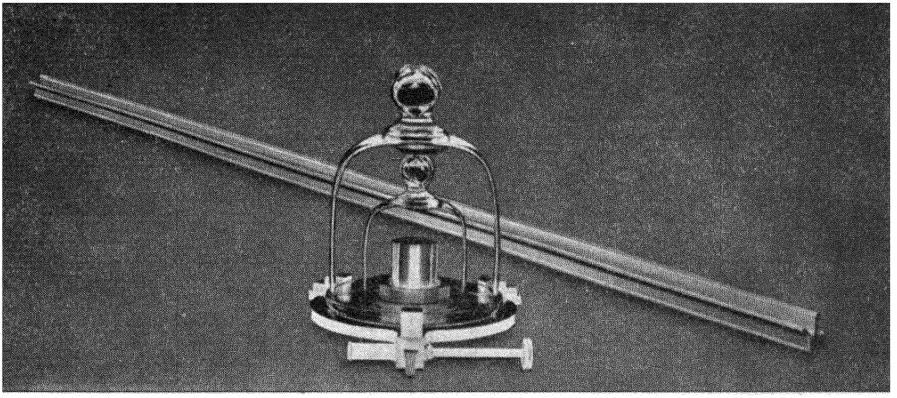


Fig. 2-8. Standard Meter and Kilogram at National Bureau of Standards These standards are exact duplicates of those at the International Bureau of Weights and Measures at Sèvres The kilogram is kept under bell jars, in a vacuum, to prevent corrosion

It was originally intended to define the kilogram so it would weigh as much as 1000 cubic centimeters, or one liter, of water at 4° C. Unfortunately, because of a slight error in setting up the standard liter, one liter is actually 1000.026 cubic centimeters. For this reason it is now the practice to use the term milliliter (ml) instead of cubic centimeter for a volume equal to $\frac{1}{1000}$ of a liter. The difference is so slight that the two may be regarded as identical for most purposes. The difference amounts to about one half a drop of water in a liter.

The Density of a Substance · An important property of a substance is its *density*, which is defined as the mass of a unit volume of the sub-

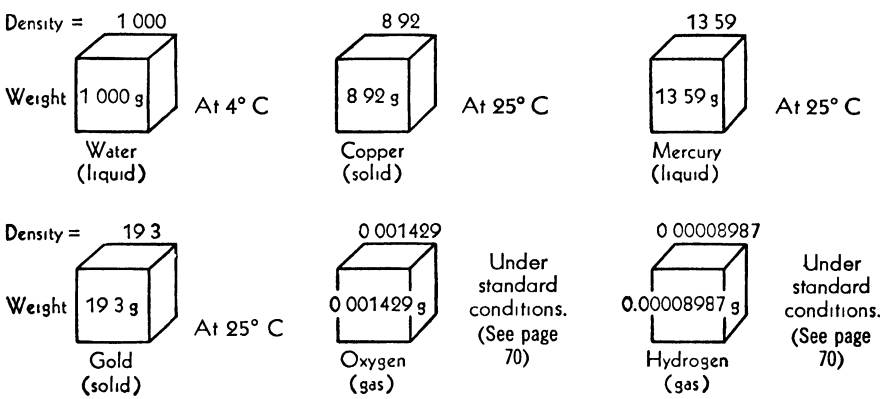


Fig. 2-9. Density, or Weight of 1 ml, of Some Well-Known Substances

stance. Since this volume of water has a mass of almost exactly 1 gram, the figures which, in the metric system, represent the density of a body, at the same time tell almost precisely how many times as heavy as water it is. Thus copper has a density of 8.92, which means that 1 milliliter weighs 8.92 grams, and also that, volume for volume, copper is 8.92 times as heavy as water. In Fig. 2-9, the densities of copper, water, mercury, and gold, and of the gases oxygen and hydrogen, are given.

Instruments to Extend Our Senses · Marvelous and delicate as our senses of sight, feeling, and hearing are, their limitations become apparent

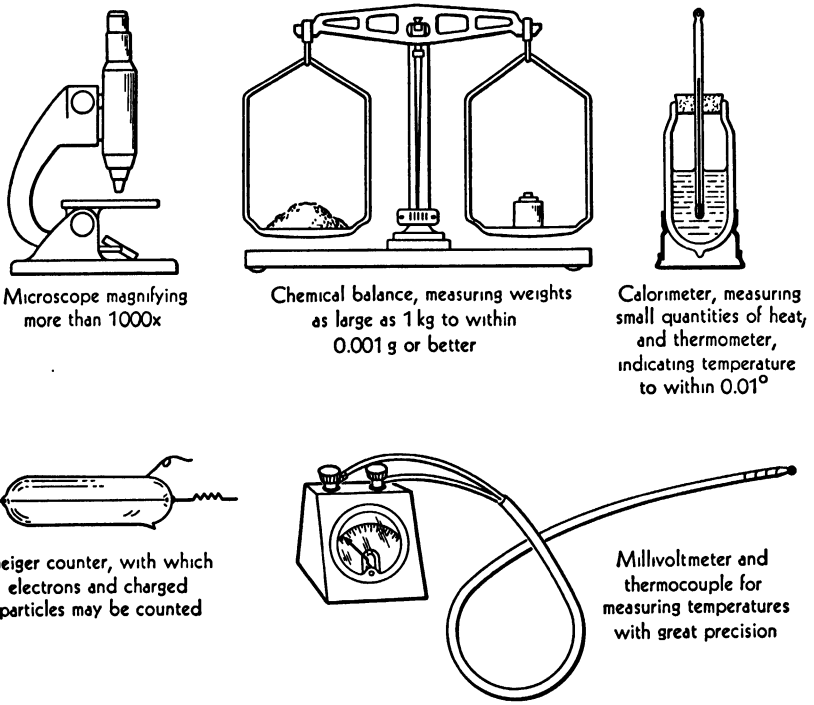


Fig. 2-10. Instruments That Extend the Senses

when we attempt to make quantitative measurements. In order to extend our senses and make our measurements more precise, we have invented and developed instruments of remarkable range and power. For example, with our unaided eye and with a linear scale like that shown in Fig. 2-3, we can measure the length of an object to within a millimeter, or even a tenth of a millimeter. But with an optical microscope the "reach" of our vision is greatly extended, so that we can observe and measure lengths down to within two ten-thousandths of a millimeter (a limit set by the wave length of light); and with an electron microscope,

particles a hundred times smaller than this come within range of vision. By means of a Geiger counter, actual single electrons and charged atoms can be counted. The tongue and upper lip and other portions of our skin are sensitive to changes of temperature and to the flow of heat; but their ability to indicate quantitatively is poor and limited indeed as compared with the power of our thermometers, thermocouples, and calorimeters. Even if it were safe to press our skin into service as a voltmeter, we should find very little usefulness in it. If we bounce an object in our hand, thus feeling its "heft," we may be enabled to guess its weight, perhaps within a few dozen grams; but with a chemical balance we can easily measure its weight to within a thousandth of a gram, or better.

The progress of science is closely associated with and very much dependent upon the invention and perfection of such instruments.

Energy

We have observed that substances in our universe are continually undergoing change. Behind or within these changes is something that causes the changes or results from the changes. We call this something energy. Without it nothing would happen; no life would exist. The changes in foods on digestion give our bodies new strength and build tissue. Changes in gasoline and air in motors drive our automobiles or make our airplanes fly. Changes in the lead and sulfuric acid in an auto battery "light" the lights or start the engine. Changes in coal in furnaces heat the air in our homes or drive locomotives. These changes all involve some form of energy.

What is Energy? · Energy, like matter, is difficult to define. Perhaps we can get a clue to a suitable definition from the common description of an active, hard-working person as "energetic," or as "a person full of energy." This common definition agrees with the scientific one: the energy of a body is the ability to do work. For example, we realize that steam, highly compressed in the boiler of a locomotive, possesses energy, or has ability to do work; for when it is admitted to the cylinder of the locomotive, it will push back the piston and move the train. Energy must be available from electric-power lines; for a motor connected with them is caused to rotate, an electric lamp to give light, a resistance heater to supply heat. Energy must be expended in raising a block of stone to the top of a building; and, when there, it too possesses energy or ability to do work, for its fall can do such things as crush rocks or drive piles into the earth.

Forms or Varieties of Energy · We recognize energy in many forms, among the most familiar of which are heat energy, electrical energy, chemical energy, radiant energy (such as that of light and electric waves), mechanical and kinetic energy (energy of moving bodies). No less important is the *potential* energy which a body possesses by virtue of its position, as when it is raised to a height, or by virtue of its existence in a state different from the equilibrium state, or in a state of strain, as in the case of a stretched spring. Potential energy, when released, may be recovered as other forms of energy.

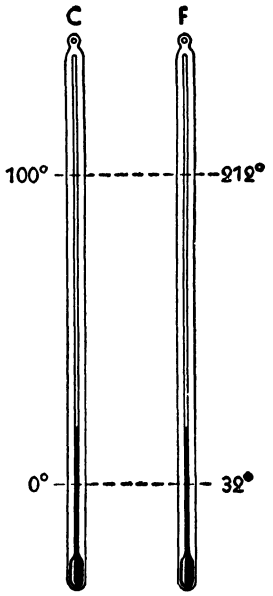


Fig. 2-11. Centigrade and Fahrenheit Scales Compared

Temperature Measurement · A change in the temperature of a substance often occurs when energy is lost or gained by the substance. This change of temperature can be detected by an instrument such as a thermometer, which is filled with a liquid whose density changes with temperature, or by a thermocouple, whose electrical properties change with temperature.

For most common uses a mercury thermometer is used. This has a bulb filled with mercury and connected to a fine tube, into which the mercury can flow as it expands when the temperature rises.

The scale of a thermometer may be one of several types. The most common scale in scientific work is the centigrade. On this scale the 0° mark is the point where the thread of mercury stands at the freezing point of water, and the 100° mark is where it stands at the boiling point of water under one atmosphere pressure.

There are other temperature scales, such as the familiar Fahrenheit scale, on which the freezing point of water is 32° and the boiling point of water under one atmosphere pressure is 212°. The relationship of the Fahrenheit to the centigrade scale is shown in Fig. 2-11. The equations for converting readings on one scale to readings on the other are as follows:

$$F° = (C° \times \tfrac{9}{5}) + 32°; \quad C° = (F° - 32°) \times \tfrac{5}{9}.$$

Later we shall be interested in another scale called the absolute scale of temperature.

Relation between Heat Energy and Mechanical Energy · In 1843 Joule arranged the apparatus shown in Fig. 2-12 so that a slowly falling weight,

attached to a cord, would cause a paddle stirrer to churn a body of water, thereby raising the temperature of the water. Joule found a constant relationship between the quantity of work performed by the falling weight and the amount of heat produced by friction in the water. This experiment, and other experiments of various kinds, have demonstrated that mechanical energy may be converted into heat and, conversely, heat into mechanical energy; and further, that there is a constant ratio between the quantities of mechanical energy and heat involved in the transformation. This is the mechanical equivalent of heat.

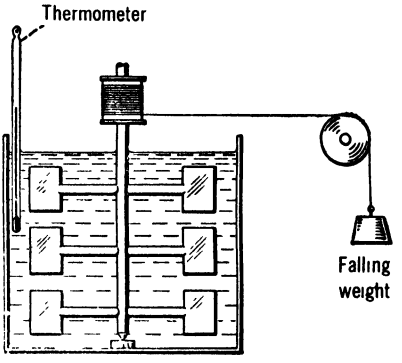


Fig. 2-12. Joule's Experiment

Other Transformations of Energy · Not only may heat and mechanical energy be interconverted, but all the various forms of energy can generally be freely transformed, one into another (Fig. 2-13). At least a part of the heat energy of burning coal can be changed into the mechanical energy of a locomotive. The kinetic energy of falling water can be trans-

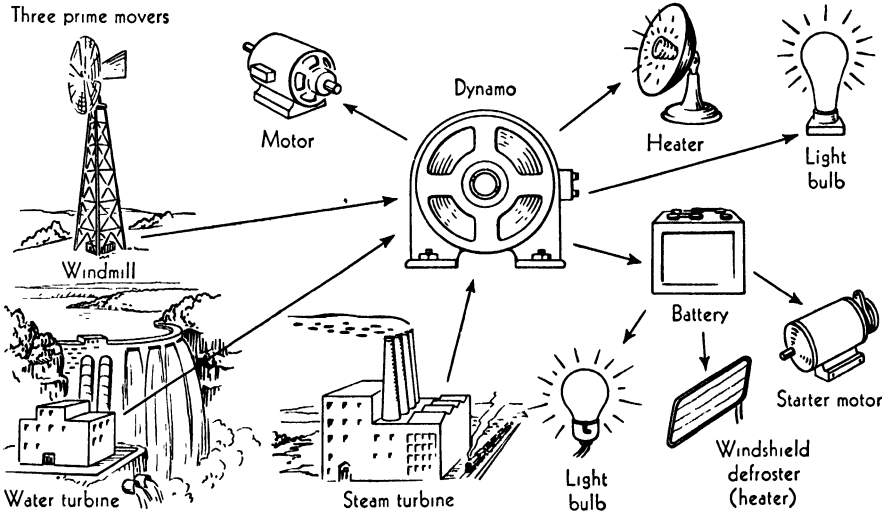


Fig. 2-13. Some Common Transformations of Energy

formed into electrical energy, made available from a trolley line, and readily converted into the kinetic energy of the moving car. In all such transformations a definite quantity of energy of one kind always gives a

definite equivalent quantity of another. Just as we speak of the mechanical equivalent of heat, we refer to the electrical equivalent of mechanical energy, or to the heat equivalent of electrical energy, or to the electrical equivalent of heat energy.

Conservation of Energy · The experimental demonstration of the complete interconvertibility, without loss, of the varieties of energy led the great German physicist Helmholtz in 1847 to formulate a law basic to both physics and chemistry, known as the *law of conservation of energy*: *Energy, like mass, in all ordinary transformations is neither created nor destroyed, but is simply transferred from one form to another, or from one body to another.*

Units of Energy · If we wish to indicate a quantity of energy, it is necessary to adopt a convenient standard for the measurement of energy. Since the various forms of energy can be transformed into heat energy, which is easily measured, we use a unit of heat energy for much of our work. The common unit of heat energy is the *calorie* (cal). It is defined as that quantity of heat which will raise the temperature of 1 gram of water 1° C at 15°. The kilocalorie (kcal) is 1000 times as large as the calorie. Another energy unit is the *British thermal unit* (Btu). It is defined as the quantity of heat required to raise 1 pound of water 1° F, and is equivalent to 252 calories.

Cgs Units of Energy · The cgs unit of energy is the *erg*. It is the energy expended, or work done, when a force of 1 dyne moves a mass of 1 gram through a distance of 1 centimeter. A *dyne* is the force which, when acting on a mass of 1 gram, will increase its velocity by 1 centimeter per second in each second. The erg is a small unit, and for many purposes it is more convenient to express energy in terms of *joules*; one joule is 10,000,000 ergs. A calorie is equivalent to 4.184 joules.

Power is the rate at which energy is expended. The practical unit of power is the *watt*, defined as the expenditure of energy at the rate of one joule per second; a *kilowatt* is 1000 watts. Electrical energy is commonly measured in kilowatt-hours—energy used at the rate of one kilowatt for one hour (or one half kilowatt for two hours, etc.). When we pay the electric company for 100 kilowatt-hours, therefore, we pay for $100 \times 1000 \times 60 \times 60 = 360{,}000{,}000$ joules, or about 86,000,000 calories, of energy.

Relationship of Matter and Energy · As already stated, the laws of conservation of matter and of energy hold for all ordinary changes and transformations. In certain unusual processes, called nuclear reactions, such as those that take place in the explosion of a fission bomb or a fusion bomb, some of the matter involved may be transformed into energy; similarly, energy may be transformed into matter. Under these condi-

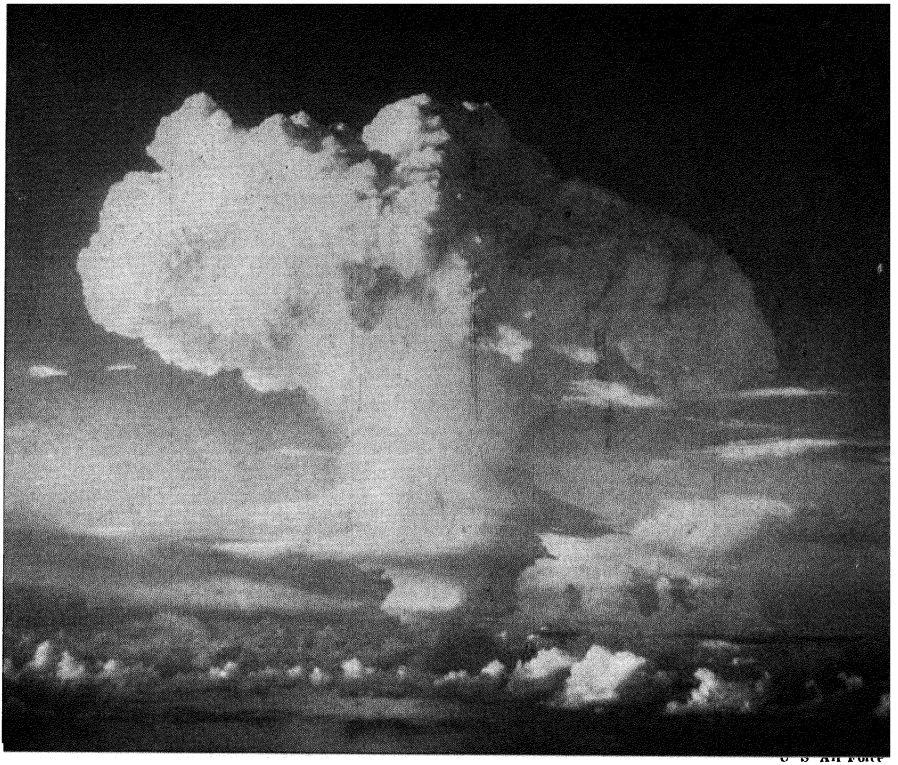


Fig. 2-14. Showing the Explosion of a Hydrogen (Fusion) Bomb · The photograph gives only a slight impression of the tremendous power of the explosion Within 2 minutes the cloud had risen to a height of 40,000 feet; within 10 minutes it had risen to 25 miles, and had mushroomed out 100 miles. The island, one of the Marshalls, disappeared completely

tions it is the sum total of matter and energy that remains constant. In 1905 Einstein suggested his famous equation for these transformations which gives us the relationship between matter and energy:

$$\text{Energy} = \text{mass} \times (\text{speed of light})^2.$$

In this equation energy is measured in ergs, mass in grams, and the speed of light in centimeters per second; and from the equation it can be calculated that 1 gram of mass transformed completely into energy would produce 9×10^{20} ergs, or 9×10^{13} joules, or 21.5 million million calories, or 25,000,000 kilowatt-hours of energy. This is equivalent to the heat produced by burning about 2500 tons of coal. This transformation of matter into energy is the source of the energy of the sun and the stars. The Einstein equation has been conclusively verified during recent years in connection with the atomic bomb (Chap. 21).

It is better, if we wish to include the extremes of our experience, to recognize that the conservation of matter and the conservation of energy are two aspects of one law, and to say that matter and energy together are conserved. In all ordinary chemical changes, the two laws hold separately.

Energy Requirements of the United States · The energy requirements for a great industrial nation are tremendous. Coal, oil, natural gas, and waterfalls are our main energy resources. The United States has about half the world's coal reserves, and produces over 60 per cent of the petroleum of the world. It is estimated that, at the present rate of increase in demand for these fuels, our common fuel reserves may be exhausted in a few centuries. Atomic fuels promise to become an important resource; one pound of uranium-238 will produce energy equivalent to 3,000,000 pounds of coal.

An interesting problem for the future is to learn how to trap solar energy and use it to heat our homes and run our engines.

QUESTIONS

1. Give definitions for (*a*) matter; (*b*) energy; (*c*) weight; (*d*) mass; (*e*) density; (*f*) chemistry.

2. Give examples of each of the following: (*a*) inertia; (*b*) a substance; (*c*) a physical property; (*d*) a chemical property; (*e*) a physical change; (*f*) a chemical change; (*g*) a very dense substance; (*h*) a substance whose density is low.

3. Do you know anything that occupies space and has no weight, or that has weight and does not occupy space?

4. Name the form of energy possessed by each of the following: (*a*) a waterfall; (*b*) wind; (*c*) electric light; (*d*) food; (*e*) a flashlight battery; (*f*) an atomic bomb.

5. Suppose the electric current in your city is produced in a steam-electric plant; enumerate the various transformations of energy from the time the coal is burned to make the steam to the time the electric current is used in your home.

6. (*a*) Define *calorie* and *British thermal unit.* (*b*) How many calories are there in 1 Btu? (*c*) What is meant by the "calorific value" of food?

7. (*a*) Why should chemistry be concerned with energy changes? (*b*) Show by means of examples how energy may be obtained more easily from some materials than from others. (*c*) What commonplace substances are important sources of energy?

8. How do you account for each of the following facts in terms of the law of conservation of mass? (*a*) A candle burns, and the material composing it entirely disappears. (*b*) A piece of iron burns, and the resulting product weighs more than the original iron. (*c*) The material in an atomic bomb "explodes," and the resulting material weighs slightly less than the original.

9. (*a*) How could the weight of a cannon ball be changed without changing its mass? (*b*) Could its mass be changed without changing its weight?

10. (*a*) All of us recognize water as a common liquid. What properties might be used to distinguish it from some other colorless liquid? (*b*) Criticize the statement "Lead is heavier than iron."

11. In what units, both cgs and English, are the following properties of matter measured? (*a*) Temperature; (*b*) weight; (*c*) length; (*d*) density.

12. Is a perpetual-motion machine possible? Why, or why not?

PROBLEMS

1. Calculate your weight in (*a*) kilograms; (*b*) grams.

2. The normal body temperature is 98.6° F. What is this on the centigrade scale?

3. Calculate your height in (*a*) meters; (*b*) centimeters.

4. Convert (*a*) 1 qt to cubic centimeters; (*b*) 1 oz to grams.

5. At a certain temperature, well below the freezing point of water, the scale readings of a centigrade and a Fahrenheit thermometer are the same. What is this temperature?

6. Refer to the table of densities in the Appendix and (*a*) calculate the volume of a diamond weighing 2.58 g. (*b*) What is its volume in cubic millimeters? (*c*) A cube of aluminum weighs 21.616 g. What is the length (cm) of the cube edge? (*d*) How many grams would a cube of gold of the same size weigh?

7. One gram of matter, if completely transformed into energy, would produce 2.15×10^{13} cal. How many tons of coal would be required to furnish this amount of heat if 1 g of the coal, when burned, produced 7400 cal?

CHAPTER 3

CHEMICAL REACTIONS; ELEMENTS, COMPOUNDS, MIXTURES

Chemical Reactions · We have already seen (p. 10) how we can recognize and identify substances by their physical and chemical properties and by the physical and chemical changes the substances will undergo. The chemist is particularly interested in chemical changes. He wants to know what happens to a candle when it burns, or to a ton of dynamite when it explodes. He has learned how to take the reddish-brown rock called hematite, mined in Minnesota, mix it with coke and limestone, heat the mixture, and obtain iron and steel. He would like, in a similar way, to produce aluminum from clay, or rayon from wood. Any specific chemical change of this sort is called a chemical reaction. A chemical reaction may be defined as *any transformation of matter which involves the disappearance of one or more substances and the appearance of one or more different substances possessing properties of their own.* Accompanying every such reaction is a characteristic energy change.

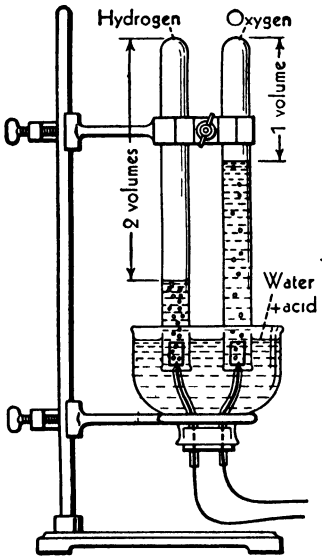


Fig. 3-1. Diagram of Apparatus for Decomposing Water by the Electric Current

It is by the careful study of such chemical reactions that the science of chemistry has been developed. We propose, in this chapter, to study several such chemical reactions. In the course of our study we shall discover certain fundamental laws of chemistry and arrive at a tentative classification of substances. We can best do this by carrying out certain experiments.

Experiment 1. The Decomposition of Water · When water is subjected to the action of a direct electric current, in the presence of a small amount of sulfuric acid, the water is decomposed. If an apparatus of the form pictured in Fig. 3-1 is used, the products of the decomposition may be collected separately, and it is found that two different gaseous substances, hydrogen and oxygen, are obtained. Each

of these gases has its own set of properties, and each is quite different from the water. It should also be pointed out that energy is *absorbed* in the decomposition. Let us write a word equation for this chemical reaction.

$$\text{Water} + \text{electrical energy} \longrightarrow \text{hydrogen} + \text{oxygen}$$

Experiment 2. Decomposition of Sugar · When a small quantity of sugar is heated in a test tube, it melts, turns brown in color, gives off vapors, and finally dries up to a solid, black residue, which is easily identified as carbon. By collecting and examining the vapors it is possible to show that they are largely water. To make this transformation of the sugar complete it is necessary to apply heat throughout the entire process. In this experiment one substance, merely by the continued application of heat, has given rise to at least two other substances of very different properties, and the change is described as a decomposition.

$$\text{Sugar} + \text{heat energy} \longrightarrow \text{carbon} + \text{water}$$

Experiment 3. The Union of Iron and Sulfur · The chief characteristics of the substances iron and sulfur are familiar to almost everyone. Iron is a dark-gray substance strongly attracted by a magnet. Sulfur is a light-yellow substance not attracted by a magnet. Sulfur is readily soluble in the liquid known as carbon disulfide; and when the solution so formed is allowed to evaporate, the sulfur is deposited in the form of yellow crystals. Iron does not dissolve in carbon disulfide.

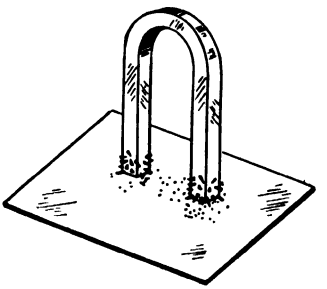


Fig. 3-2. Sulfur Is Not Attracted by the Magnet. But Iron Is Attracted and Can Be Completely Removed from the Mixture

When iron and sulfur are thoroughly ground together, a greenish-gray powder is obtained which appears to be quite different from either of them; but when we test for the presence of these two materials, we find that in many respects the powder acts like these two taken separately. Carbon disulfide dissolves the sulfur but not the iron. A magnet rubbed through the powder withdraws the iron and leaves the sulfur unchanged (Fig. 3-2). Both the sulfur and the iron have the set of properties which they had before they were ground together; they are said to constitute a *mixture*.

If now a portion of the mixed powder is placed in a test tube and heated (Fig. 3-3), it soon begins to glow, at the point of greatest heat. Even if the flame is withdrawn, the glow spreads throughout the entire contents of the test tube, and a great deal of heat energy is set free. When the material in the test tube is cooled and examined, it is found that the

distinguishing characteristics of the iron and sulfur have disappeared. Carbon disulfide no longer dissolves the sulfur and leaves the iron; a magnet has no effect upon the material.

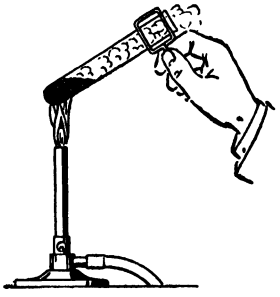


Fig. 3-3. Heating a Mixture of Iron and Sulfur

This product differs entirely from its constituents in its properties, such as density, color, hardness, solubility, and melting point. This new material is called *iron sulfide.*

Iron + sulfur ⟶ iron sulfide + energy

Some Generalizations That Can Be Made After a Study of These Chemical Reactions · Let us assemble the word equations for the chemical reactions we have described and examine them in somewhat more detail. We shall find it possible to make certain generalizations.

Water + energy ⟶ hydrogen + oxygen
Sugar + energy ⟶ carbon + water
Iron + sulfur ⟶ iron sulfide + energy

1. **Substances may be simple or complex.** If we examine these chemical reactions further we can see that certain of the substances involved are complex. For example, water must be made up of at least two substances, hydrogen and oxygen, since these two are formed when water is decomposed. In the same way we can reason that iron sulfide must consist of at least two simpler substances, since it is formed by the union of iron and sulfur. Sugar must be made up of at least three substances, since it forms carbon and water when it decomposes, and water has been shown to be composed of hydrogen and oxygen.

The question now arises: Is there any substance which cannot be broken up into simpler substances? Many years of experiment and experience have shown that there are about a hundred substances which cannot be broken up, by any chemical means, into simpler substances. These substances are known as *elements.* The list of elements includes carbon, oxygen, hydrogen, iron, and sulfur in the examples we have used; and others, such as gold, silver, copper, lead, nitrogen, phosphorus, and calcium.

If carbon, oxygen, hydrogen, sulfur, and iron are called elements, how shall we classify those more complex substances such as water, sugar, and iron sulfide, which are made up of elements? These substances are known as *compounds*; but let us postpone an attempt to define the term *compound* until we have obtained some additional information from further study of the three chemical reactions.

2. Chemical reactions take place between definite quantities of materials. If we mix 4 grams of sulfur with 7 grams of iron and allow them to react, as in Experiment 3, above, we obtain 11 grams of iron sulfide (Fig. 3-4). The question now arises, should we obtain more iron sulfide if we mixed more sulfur—7 grams instead of 4—with 7 grams of iron? Experiments have shown that the answer to this question is No! In such a case we still obtain 11 grams of iron sulfide, and have 3 grams of sulfur left over. In fact, there is an enormous amount of evidence that chemical reactions always take place in definite ratios by weight. For the three reactions that we are studying, the simplest ratios, by weight of reactants and products, are shown in the following equations:

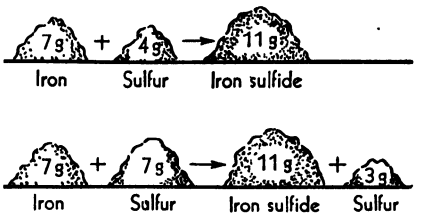


Fig. 3-4. Illustrating the Definiteness of Chemical Reactions

$$\underset{9\text{ g}}{\text{Water}} + \text{energy} \longrightarrow \underset{1\text{ g}}{\text{hydrogen}} + \underset{8\text{ g}}{\text{oxygen}}$$

$$\underset{19\text{ g}}{\text{Sugar}} + \text{energy} \longrightarrow \underset{8\text{ g}}{\text{carbon}} + \underset{11\text{ g}}{\text{water}}$$

$$\underset{7\text{ g}}{\text{Iron}} + \underset{4\text{ g}}{\text{sulfur}} \longrightarrow \underset{11\text{ g}}{\text{iron sulfide}} + \text{energy}$$

The Law of Definite Composition · As we have seen in the case of the combination of iron and sulfur in the previous section, elements combine with each other in fixed proportions by weight. Thus, iron sulfide contains the elements in the ratio of 7 (actually 6.98) parts iron to 4 (actually 4.01) parts sulfur. Furthermore water, which always decomposes to give 8 parts by weight of oxygen to 1 (actually 1.008) of hydrogen, must be made up of oxygen and hydrogen in this fixed ratio. These facts are summarized by the statement that *in a pure compound, the several elements are always combined in a definite ratio by weight.* This statement is known as the *law of definite composition.*

3. Energy is either absorbed or liberated in a chemical reaction. In one of the reactions described, the union of iron and sulfur, energy was liberated in the form of heat. In the other two reactions, energy was absorbed. In the case of the decomposition of water the energy absorbed was electrical energy; in the case of the decomposition of sugar the energy absorbed was heat energy. It is characteristic of all chemical reactions that some change in energy takes place, and that the amount of energy absorbed or liberated is perfectly definite, as definite as the amounts of

reactants and of products. For example, 6.98 grams of iron reacts with 4.01 grams of sulfur to give 10.99 grams of iron sulfide, liberating about 2880 calories of heat; while it requires about 143,000 volt-coulombs of electrical energy (equivalent to about 34,200 calories of heat) to decompose 9.008 grams of liquid water into 8.000 grams of oxygen gas and 1.008 grams of hydrogen gas.

The fact that energy is absorbed or liberated in the course of chemical reactions would seem, at first glance, to controvert the law of conservation of energy. However, that is not the case. The energy set free when iron and sulfur react already existed in the iron and sulfur, as a special form of potential energy called *chemical energy*, and the energy absorbed in decomposing water is merely changed to chemical energy.

4. **Chemical compounds are made up of elements.** We have seen that chemical changes result in changes in properties, that they occur between definite amounts of substances, and that the energy changes associated with the reactions of these definite amounts are also perfectly definite. With this information we are now ready to define a chemical compound. *A chemical compound is a substance made up of two or more elements, in definite proportions by weight, having properties different from those of the elements of which it is composed.*

Elements Can Combine in More than One Ratio · We have said, in the preceding pages, that elements react in definite proportions by weight to form compounds. While every chemical compound contains its elements in definite ratios by weight, it is possible for the same elements to react in two or more different ratios to form two or more different compounds. For example, carbon and oxygen may unite in two different ratios to form the two compounds, carbon monoxide and carbon dioxide. (Carbon monoxide is the poisonous gas sometimes found in the exhaust gases from an automobile engine. Carbon dioxide is nonpoisonous, and is a normal constituent of the air.) We can write word equations for the reactions by which these two compounds are formed, as follows:

$$\overset{3}{\text{Carbon}} + \overset{4}{\text{oxygen}} \longrightarrow \overset{7}{\text{carbon monoxide}}$$

$$\overset{3}{\text{Carbon}} + \overset{8}{\text{oxygen}} \longrightarrow \overset{11}{\text{carbon dioxide}}$$

If we examine the ratios by weight by which carbon and oxygen combine to form these two compounds, we note that the amount of oxygen combined with 3 parts of carbon in the second reaction is exactly twice that combined with 3 parts of carbon in the first reaction. Examination of a number of cases in which the same elements have combined to form

different compounds gives rise to the generalization that *if the same elements A and B form more than one compound, the weights of A combined with a fixed weight of B in the compounds are in the ratio of whole numbers which are usually small.* This generalization is known as the *law of multiple proportions.*

Forming a Theory about the Structure of Matter · In the past few pages we have been following the *scientific method* (p. 6). In each case, in step I we collected a series of facts; in step II we used these facts to formulate certain generalizations or laws: the Law of Conservation of Mass, the Law of Definite Composition, and the Law of Multiple Proportions. Now, in step III, we are ready to propose a theory to explain these facts and laws; and later, in step IV, we shall test the theory.

Is Matter Made Up of Particles? The early philosophers often debated the question "Is matter continuous and infinitely divisible, or is every substance made up of great numbers of unit particles?" Many argued that there is no lower limit to the size of a piece of any substance. To others it seemed more reasonable to believe that if a small piece of iron or sulfur, for example, were to be divided and then subdivided a great many times, a particle would finally be found which could not be further divided without loss of all the properties of iron or of sulfur. These early philosophers had no direct evidence for either of their theories, and the question was not settled until the experimental approach to science made possible the development of the laws of definite composition and multiple proportion. When these laws were discovered, it became increasingly apparent that the theory that matter is made up of elementary particles could explain the laws, while the theory that matter is infinitely divisible could not explain them.

It remained for the English scientist, John Dalton (Fig. 3-5), to show that if these minute particles, which we call atoms, were endowed with fixed and definite weights, then all the facts expressed by the laws describing weight relationships in chemical combinations could be explained. The formulation of the *atomic theory* by Dalton in 1806, describing particles which neither he nor anyone else had ever seen individually, represents one of the triumphs of the mind of man in interpreting natural phenomena. As science has advanced, the clarity and reasonableness of interpreting chemical phenomena in terms of the concept of atoms has been shown again and again.

The Atomic Theory · A summary of the main points of the atomic theory as proposed by Dalton and accepted today is as follows:

a. All matter is made up of unit particles called atoms.

b. The atoms of a particular element have the same weight, or at least

an average weight characteristic of that element; atoms of different elements have different average weights.

c. In chemical reactions whole atoms, never fractions of atoms, combine or separate, or change places.

d. When atoms combine with other atoms they do so in one or more whole-number ratios which are usually small.



Fig. 3-5. John Dalton (1766–1844) An Englishman famous as a teacher and scientist. He made many studies on the properties and composition of gases, but his greatest contribution to science was his development of the atomic theory. He wrote an important book entitled *A New System of Chemical Philosophy*, which exerted a great influence upon the development of chemistry.

Use of the Atomic Theory · The idea that matter is made up of atoms explains several observations we have made in this chapter.

1. **Elements and compounds can be defined in terms of atoms.** An element is a substance made up of one kind of atom only; a compound is a substance made up of two (or more) different kinds of atoms in chemical combination. Thus the element hydrogen has only atoms of hydrogen, but the compound water is made up of hydrogen atoms and oxygen atoms united chemically.

2. **The law of definite composition can be explained in terms of atoms.** When water is decomposed, 9 grams of water always gives 8 grams of oxygen and 1 gram of hydrogen. Let us assume that each unit particle of water (called a molecule) consists of a definite number of atoms of hydrogen combined with a definite number of atoms of oxygen; for example, two atoms of hydrogen and one of oxygen; and that the weight of an oxygen atom is 16 times that of a hydrogen atom. It follows that there is 8 times as much oxygen, by weight, in the molecule as there is hydrogen (although there are twice as many hydrogen atoms). Since any quantity of water is simply a collection of molecules, the composition of water is the same as the composition of the molecule: eight times as much oxygen as hydrogen; and is perfectly definite.

3. **The law of multiple proportions can be explained by the atomic theory.** Here we have the crucial test of the atomic theory. We learned

(p. 26) the very interesting fact that when two elements form more than one compound the weights of the one element which combine with a fixed weight of the other are in the ratio of small whole numbers. This must mean that the *number* of atoms of one element which combine with a given *number* of atoms of the other may be different. This will appear in the following example:

Example. We saw (p. 26) that carbon forms two oxides, carbon monoxide and carbon dioxide, and that the weights of oxygen combined with 3 g of carbon in the two oxides are respectively 4 g and 8 g. Let us assume that a unit particle (molecule) of carbon monoxide consists of one atom of carbon and one of oxygen (CO), and that the molecule of carbon dioxide consists of one atom of carbon and two of oxygen (CO_2). It follows that the weight of oxygen combined with one atom of carbon in carbon dioxide is twice the weight of oxygen combined with one atom of carbon in carbon monoxide; and since any large quantities of these two compounds are merely collections of the respective molecules, the weights of oxygen combined with a fixed weight of carbon in the two compounds will always be in the ratio of 2 to 1



Fig. 3-6. Illustrating the Law of Multiple Proportions
Dalton's models of molecules of carbon monoxide (CO) and carbon dioxide (CO_2)

Testing and Confirming the Atomic Theory · Step IV in the scientific method of reasoning (p. 7) consists in testing the theory experimentally. When Dalton first proposed his theory, it met with some measure of belief and considerable disbelief. The only answer was, of course, to design experiments to check the theory. Many such experiments have been carried out, including careful checking of the laws of definite composition and multiple proportion. The results have established the theory beyond any reasonable doubt, and we can accept it as truth.

Chemist's Method of Indicating Elements, Compounds, and Chemical Reactions · The chemist makes use of the ideas of the atomic theory in developing a species of shorthand characters to indicate the composition of substances and the changes they undergo.

1. **Elements are designated by symbols.** For each element we use some suitable abbreviation to stand for the atom of element, much as we abbreviate the names of our states. Thus H is the symbol for the atom of hydrogen, and O is the symbol for the atom of oxygen. Because several names begin with the same letter, it is often necessary to add a second letter to the first. Thus C stands for the atom of carbon, Cl for that of chlorine, and Ca for that of calcium. It should be noted that the first letter of a symbol is capitalized; the second letter is a small letter. In some cases a symbol is an abbreviation of an old Latin name

of the element. In this way Fe stands for the atom of iron (*ferrum*), Cu for that of copper (*cuprum*), and Hg for that of mercury (*hydrargyrum*).

When chemists wish to refer to an element, they use the full name of that element, not the abbreviation. A chemist does not say, "This sealed flask contains He." What he says is "This sealed flask contains helium." The word helium refers to the substance itself, regardless of quantity. The quantity may be large or small; helium may refer even to a single atom. But the symbol He is reserved for use when one expressly wishes to refer to a definite quantity of helium; this may be a single atom or a very special number of atoms of the element (see Chapter 9).

2. **Compounds are designated by formulas.** Since the molecule of water has been found to consist of two atoms of hydrogen and one of oxygen, we may indicate the water molecule by the combination of symbols H_2O, in which the subscript 2 refers to the symbol just preceding it. This is spoken as if it were spelled out "H-two-O," and is called the *formula* of the water molecule. The formula is a group of symbols which gives the kind and number of atoms in a molecule. Similarly FeS is the formula for iron sulfide, since experiment has shown this compound to consist of iron (Fe) and sulfur (S) in the ratio of one atom of iron to one atom of sulfur.

If we wish to indicate a certain number of molecules, we write that number before the formula. Thus $2\ H_2O$ represents two molecules of water; $3\ CO_2$, three molecules of carbon dioxide. The expression 2 H indicates two uncombined atoms of hydrogen; H_2 represents a molecule of hydrogen consisting of two atoms.

3. **Chemical reactions are indicated by means of chemical equations.** Earlier in our discussion of chemical changes we used a device called a word equation to indicate the chemical change. Word equations can be made more precise and informative by using the symbols and formulas of the elements and compounds involved. For example, the decomposition of water by the electric current is represented by the equation:

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

This shows that when water is so decomposed, two molecules of water yield two molecules of hydrogen and one molecule of oxygen. Since we know that the molecules of hydrogen and oxygen consist of two atoms each and not of separate atoms, it is not correct to write

$$H_2O \longrightarrow 2\ H + O$$

The union of iron and sulfur to form iron sulfide is expressed by the equation

$$Fe + S \longrightarrow FeS$$

This states that one atom of iron combines with one atom of sulfur to form iron sulfide.

It should be clearly understood that all such formulas and equations are simply a method of stating experimental facts. The experimental facts are obtained first; then we record them in abbreviated form by writing formulas and equations. The formulas express the composition of compounds, and the equations show how the compounds react with one another. The methods by which we determine these correct formulas and equations from the experimental facts will be explained in detail in later chapters (Chaps. 9, 10).

The chemical equations corresponding to the word equations for the reactions studied in this chapter are as follows:

$$\underset{2\,H_2O}{\text{Water}} \xrightarrow{\text{electrolyzed}} \underset{2\,H_2 \;+\; O_2}{\text{hydrogen} + \text{oxygen}}$$

$$\underset{C_{12}H_{22}O_{11}}{\text{Sugar}} \xrightarrow{\text{heated}} \underset{12\,C \;+\; 11\,H_2O}{\text{carbon} + \text{water}}$$

$$\underset{Fe \;+\; S}{\text{Iron} + \text{sulfur}} \longrightarrow \underset{FeS}{\text{iron sulfide}}$$

$$\underset{C \;+\; O_2}{\text{Carbon} + \text{oxygen}} \longrightarrow \underset{CO_2}{\text{carbon dioxide}}$$

$$\underset{2\,C \;+\; O_2}{\text{Carbon} + \text{oxygen}} \longrightarrow \underset{2\,CO}{\text{carbon monoxide}}$$

Distribution of the Elements · Our direct knowledge of the earth's composition is limited to what is really a very thin surface crust only a

ELEMENTS IN THE EARTH'S CRUST, THE OCEAN, AND THE ATMOSPHERE

	SOLID 10-MILE CRUST, 93 PER CENT	OCEAN, 6.91 PER CENT	AVERAGE, INCLUDING ATMOSPHERE
Oxygen	46.71	85.79	49.52
Silicon	27.69		25.75
Aluminum	8.07		7.51
Iron	5.05		4.70
Calcium	3.65	0.05	3.39
Sodium	2.75	1.14	2.64
Potassium	2.58	0.04	2.40
Magnesium	2.08	0.14	1.94
Hydrogen	0.14	10.67	0.88
Titanium	0.62		0.58
Phosphorus	0.130		0.120
Carbon	0.094	0.002	0.087
Chlorine	0.045	2.07	0.188
Other elements	0.391	0.098	0.295
	100.00	100.00	100.00

few miles in thickness. Relative to the diameter of the earth, this shell is no thicker than the skin on a large apple. The table on page 31, prepared by F. W. Clarke and based on analyses of representative rocks, sea water, and air, with estimates of their quantities, indicates the approximate composition of this crust. It will be seen that 13 of the elements are estimated to constitute 99.705 per cent of the total, while the others make up the remaining 0.295 per cent. Some of these elements are so rare that our entire acquaintance with them is limited to a few grams or even less.

Elements Essential to Life · The following table, compiled by Sherman, indicates the relative amounts of various elements in the human body:

AVERAGE COMPOSITION OF THE HUMAN BODY

	PER CENT		PER CENT
Oxygen	65.00	Sulfur	0.15
Carbon	18.00	Chlorine	0.15
Hydrogen	10.00	Magnesium	0.05
Nitrogen	3.00	Fluorine	Very
Calcium	1.50	Silicon	minute
Phosphorus	1.00	and other elements	amounts
Potassium	0.35		

The list of "other elements" mentioned in this table includes iron, copper, zinc, manganese, cobalt, iodine, boron, and molybdenum. The first six of these are essential to animals. The first four and the last two are necessary to plants. The exact physiological role of these elements that are found in the body and in plants in mere traces is not well known, but they seem to be intimately connected with the functioning of vitamins and enzymes and other agents that modify and control the rate of chemical reactions in living organisms.

QUESTIONS

1. Give precise definitions of (*a*) mixture; (*b*) element (preferably in terms of atoms); (*c*) compounds; (*d*) atom.

2. Could you have a mixture of elements? a mixture of compounds? a mixture of an element and a compound?

3. List by names ten elements and ten common compounds that you have observed and with which you have come in contact.

4. Indicate which of the following substances are homogeneous, and which are heterogeneous: (*a*) wood; (*b*) sugar; (*c*) water; (*d*) iron; (*e*) rust; (*f*) brass; (*g*) granite; (*h*) coin silver; (*i*) molasses; (*j*) wine; (*k*) brick; (*l*) glass; (*m*) air; (*n*) salt; (*o*) mercury; (*p*) coal. State your reasons.

5. Of the substances listed in Question 4, which are elements? compounds? mixtures?

6. The early Greek philosophers thought that earth, air, fire, and water were all elements. We no longer consider them such. How would you classify each of them?

7. Aluminum is a more abundant element than iron. Why, then, is aluminum metal more expensive than iron?

8. When iron and sulfur react, iron sulfide is formed and heat is evolved:

$$\text{Iron} + \text{sulfur} \longrightarrow \text{iron sulfide} + \text{heat}$$

a. Using the law of conservation of mass and the law of conservation of energy, what can you say about each of the following?

1. The relationship between the weights of iron, sulfur, and iron sulfide.
2. The chemical energy of iron + sulfur as compared with that of iron sulfide.

b. Suppose that, in two separate experiments, you mixed (1) 50 g of iron and 25 g of sulfur, and (2) 25 g of iron and 50 g of sulfur, and started the two reactions. Would the composition of the resulting iron sulfide differ in the two cases?

9. What commonplace evidence can you cite in support of the belief that matter is not continuous but is made up of particles?

10. Iron and chlorine form two compounds. The amounts of iron combined with a given amount of chlorine are in the ratio of 1 : 1.5 (2 : 3). Explain this fact in terms of atoms of iron and chlorine.

PROBLEMS

1. Iron sulfide contains 63.52 per cent of iron and 36.48 per cent of sulfur. (*a*) How much iron is present in 500 g of iron sulfide? (*b*) How many pounds of iron could be recovered from 1 ton of iron sulfide if the recovery were complete? (*c*) How many grams of sulfur react with iron in the formation of 2500 g of iron sulfide?

2. Two compounds of lead with oxygen have the following compositions:

I. lead 92.83%, oxygen 7.17%
II. lead 86.62%, oxygen 13.38%

(*a*) Calculate the weight of oxygen combined with one gram of lead in each of the compounds. (*b*) Are these amounts of oxygen in the ratio of one small whole number to another? (HINT. Divide the larger number by the smaller.) If so, what is this ratio?

CHAPTER 4

ABOUT ATOMS

In this chapter we shall give the answers to such questions as these about atoms:

1. How big are atoms?
2. How much do atoms weigh?
3. Are atoms really the simple particles of matter that Dalton thought?
4. How do atoms combine with each other?

Answers to these questions will help us to understand better the formation of compounds and the properties of the elements and compounds to be studied in the next dozen chapters. We shall consider this discussion as a preview of the atom.

Later (Chap. 19) we shall be ready to make a more thorough study of the experimental evidence upon which much of the present discussion is based.

How Big Are Atoms? · The atoms are extremely small, spherical particles, approximately 0.000,000,01 centimeter (or 10^{-8} cm) in diameter. This means that they are about one thousand times smaller than the smallest particle (0.000,01 cm, or 10^{-5} cm) that can be distinguished clearly with the most powerful optical microscope.

It is often convenient in stating the size of atoms to use a unit of measurement of the same order of magnitude as the diameters of the atoms. This unit is the angstrom unit (Å) which is equal to 0.000,000,01 cm (or 10^{-8} cm). Atoms of the different elements vary in size from about 1 Å to 5 Å in diameter.

Many schemes have been devised to help us to realize how tiny atoms really are. For example, it would require about 4,000,000 iron atoms (diameter about 2.5×10^{-8} cm) in a line, atom touching atom, to reach across the head of a pin, a distance of about 1 mm.

How Much Do Atoms Weigh? · A particle as small as an atom may be expected to have a very small weight. The weights of several atoms of different elements are given in the table at the top of page 35.

The weights are much smaller than can be detected with the most sensitive balance (sensitive to about 0.000,01 g); but there are methods of determining them very precisely. These methods will be explained in Chapter 9.

THE WEIGHTS OF SEVERAL ATOMS

ELEMENT	WEIGHT OF AN ATOM	RELATIVE WEIGHT
Hydrogen . .	0.000,000,000,000,000,000,000,001,67 g, or 1.67×10^{-24} g	1.008
Oxygen	0.000,000,000,000,000,000,000,026,6 g, or 26.6×10^{-24} g	16.000
Chlorine . . .	0.000,000,000,000,000,000,000,058,9 g, or 58.9×10^{-24} g	35.457
Uranium . . .	0.000,000,000,000,000,000,000,395 g, or 395.0×10^{-24} g	238.07

The chemist is seldom interested in the absolute weight of an atom, but needs to know its *relative weight* (last column of the table above); and there are reliable methods for determining the relative weights accurately, even without knowing the absolute weights of the single atoms. The relative weights are called *atomic weights.*

Are Atoms Really the Simple Particles of Matter That Dalton Thought? · For almost 100 years after Dalton proposed the atomic theory, chemists and physicists were content to look upon the atoms as hard, elastic, round, dense, unchanging particles. Not until about 1900 was it clearly realized that this is not true.

Today much evidence has been gathered which convinces us that atoms are not hard, round, dense particles as Dalton thought. Instead each atom is a system which comprises a dense core or *nucleus*, surrounded at relatively great distances by other particles, the latter moving in orbits about the nucleus (Fig. 4-1). Nearly all the mass of the atom is concentrated in the nucleus, but the volume of the atom is determined by the outermost orbits. Thus an atom is in some respects like a miniature solar system, with a central sun and its satellites.

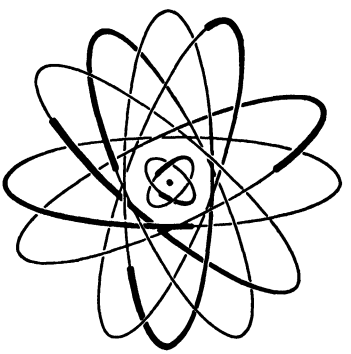


Fig. 4-1. Illustrating Theory of Structure of the Oxygen Atom · Showing the nucleus surrounded by two inner and six outer electron orbits

It has been shown further that the nucleus always carries a positive electrical charge. In fact, the fundamental difference between atoms of different elements lies in the magnitude of this charge (see atomic number, p. 37).

The concept of atomic structure presented above raises many questions: "How does the nucleus get its charge?" "Why is the atom electrically neutral, if it carries this charge on the nucleus?" "What gives an atom its mass?" The following brief outline summarizes the facts and theories about atomic structure as they have been discovered and developed in the last half-century.

The Building Units of Atoms · Atoms are made up of three smaller particles: electrons, protons, and neutrons. Some of the properties of these particles are given in the following table.

THREE PARTICLES IN THE MAKE-UP OF ATOMS

NAME	CHARGE	MASS (O = 16 000)
The proton (p)	Positive by 1 unit	1.007582
The neutron (n)	No charge	1.00893
The electron (e^-)	Negative by 1 unit	0.000549

NOTE. At times other particles appear, particularly in certain nuclear changes. Whether these particles (mesons, positrons, neutrinos, etc.) are actually a part of the atomic structure or are formed in the course of nuclear changes is still a debatable question.

1. **The electron.** About 1900 J. Thomson demonstrated that tiny particles carrying negative electric charges could be obtained from all atoms. These particles are called electrons. Thomson was able to measure the ratio of the charge on the electron to the mass of the electron. By further work Millikan was able

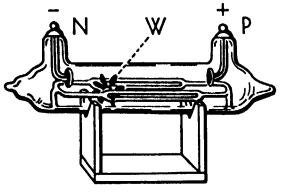


Fig. 4-2. Apparatus to Show that Negatively Charged Particles (Electrons) Carry Electricity through a Vacuum The plate *N* is made negative; the electrons streaming from it strike against the paddles on the wheel *W* on their way to the positive plate *P*. The wheel revolves and rolls toward *P*. The motion of the wheel shows that *particles* are striking it. The direction of motion shows that these particles are repelled by the negative plate and attracted by the positive plate; hence they are *negatively charged*

to prove that each electron carried the same charge, which amounts to 1.602×10^{-19} coulomb, the unit charge referred to in the table. From the results of Thomson and Millikan it was possible to calculate the mass of the electron, which is found to be approximately $\frac{1}{1837}$ that of the hydrogen atom.

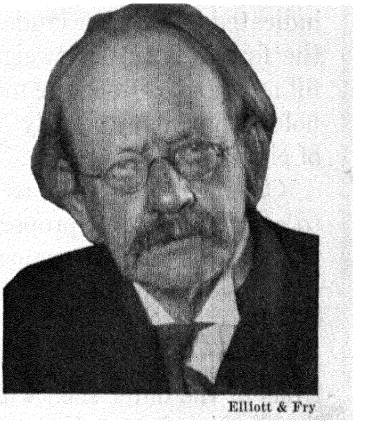
The electron, then, is a particle of negative electricity, of definite charge and mass, which is a universal constituent of matter and which in suitable multiples makes up all negative electrical charges. Each atom is neutral, because it contains enough electrons to balance the positive charge on the nucleus.

2. **The proton.** Because matter is electrically neutral, physicists searched for a positively charged particle corresponding to the electron in charge. When the positive particle was isolated, its charge proved to be equal to that of the electron but opposite in sign. But its mass was nearly equal to that of the hydrogen atom, namely to $\frac{1836}{1837}$ of that weight. This positive particle was called the proton.

3. **The neutron.** In 1932 Chadwick discovered the neutron, a third atomic component (above). As the name indicates, the neutron is electrically neutral; its mass is almost the same as that of a proton. Neutrons make up about half of the weight of most of the atoms.

How Are These Particles Arranged in Atoms? · The discovery that all atoms are composed of three simple particles raises the question why atoms are different. Evidently atoms must differ from each other either in the number of particles or in their arrangement, or both.

1. **The nucleus.** The nucleus of an atom is very much smaller (about one hundred thousand times smaller) than the atom, of which it is the central core; but nearly all the weight of an atom resides there. In the nuclei of all atoms are protons, particles carrying one positive electric charge. In the nucleus of the lightest atom (hydrogen) there is one proton; in the next heavier (helium) there are two protons; in the next (lithium) three; and so on, through the whole list of elements (*nearly* one hundred). For example, uranium, the ninety-second, has ninety-two protons in its nucleus. The number of protons in the nucleus determines the charge on the nucleus, which is called the *atomic number.*



Elliott & Fry

Fig. 4-3. Sir Joseph Thomson (1856–1940) Formerly director of the Cavendish Laboratory, Cambridge, England

Also present in the nucleus (except in ordinary hydrogen) is the *neutron,* having nearly the same weight as the proton, but carrying no charge. The protons and neutrons are present in about equal numbers, although the neutrons predominate somewhat in the heavier atoms. The proton gives the positive charge to the nucleus of the atom; for example, 92+ to uranium. The protons and neutrons together contribute most of the weight of the atom; their sum is approximately the atomic weight.

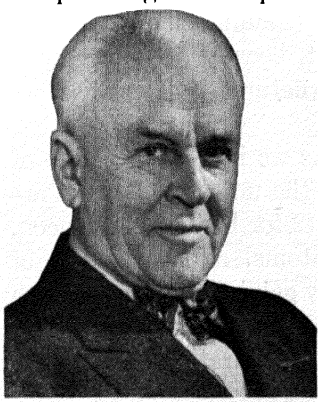


Fig. 4-4. Robert A. Millikan (1868–1953) · Formerly director of the Physical Laboratory, California Institute of Technology

Since the protons and neutrons in the nucleus are packed together into a very tiny space, the density of the nucleus is very great. It is about 10^{13} grams per cubic centimeter. This means a mass of nuclear material about the size of the end of one's thumb would weigh about 60,000,000 tons.

2. **Outside the nucleus.** The region of an atom outside the nucleus is practically empty space, which is patrolled by electrons. These contribute very little weight to the

atom; but they neutralize the charge of the protons, and the outermost area in which they move determines the size of the atom. The normal atom is neutral electrically, and the number of the electrons (−) surrounding the nucleus is the same as the number of protons (+) in the nucleus.

Electron Levels · The electrons occupy spherical shells, or levels, as indicated in a rather crude and diagramatic way in Fig. 4-5, representing the first twenty, lightweight elements. It will be noted that the levels fill as the atoms acquire more electrons. The innermost electron shell can hold a maximum of only two electrons, and the next shell a maximum of eight.

Chemical properties, as well as physical properties, change from atom to atom. Chemical properties depend especially on the number of electrons in the very outermost shell; and elements made up of atoms with the same number of electrons in the outer shell have similar properties. This is emphasized in Fig. 4-5 by arranging the atoms in eight columns, according to the number of electrons in the outer shells. It is the electrons in the outer shell which take part in chemical reactions.

Chemists have adopted a simplified scheme. The symbol of the atom is allowed in this scheme to represent the nucleus and all the electrons except those in the outside shell; and the outermost electrons are represented by dots. For example, the atoms of sodium, chlorine, carbon, oxygen, and hydrogen may be represented as follows:

$$\dot{\mathrm{Na}} \quad :\ddot{\underset{\cdot}{\mathrm{Cl}}}: \quad \cdot\dot{\underset{\cdot}{\mathrm{C}}}\cdot \quad :\ddot{\underset{\cdot\cdot}{\mathrm{O}}} \quad \mathrm{H}\dot{}$$

How Do Atoms Combine with Each Other? · We know that hydrogen atoms combine with oxygen atoms to form water; that sodium atoms react with chlorine atoms to form table salt (sodium chloride); that atoms of helium, neon, and argon do not react, because they are inert. What features or patterns in the electron structures can we discover which give us an explanation of these facts?

Some Atoms Are Stable and Unreactive · As we inspect the table of electron configuration (Fig. 4-5), we note that the unreactive atoms are those that have outside shells which are filled (2 for helium, 8 for neon, and 8 for argon). Such filled shells give stable atoms. Atoms that do not have filled shells can attain this configuration by gaining or losing enough electrons or sharing enough pairs of electrons to leave the atoms with filled shells. This tendency to attain a stable configuration seems to be the driving force of chemical reactions.

Some Atoms React by Gaining or Losing Electrons · Certain atoms may gain or lose electrons, thereby acquiring an electrical charge. For example, a sodium atom may give up the single electron in its outside

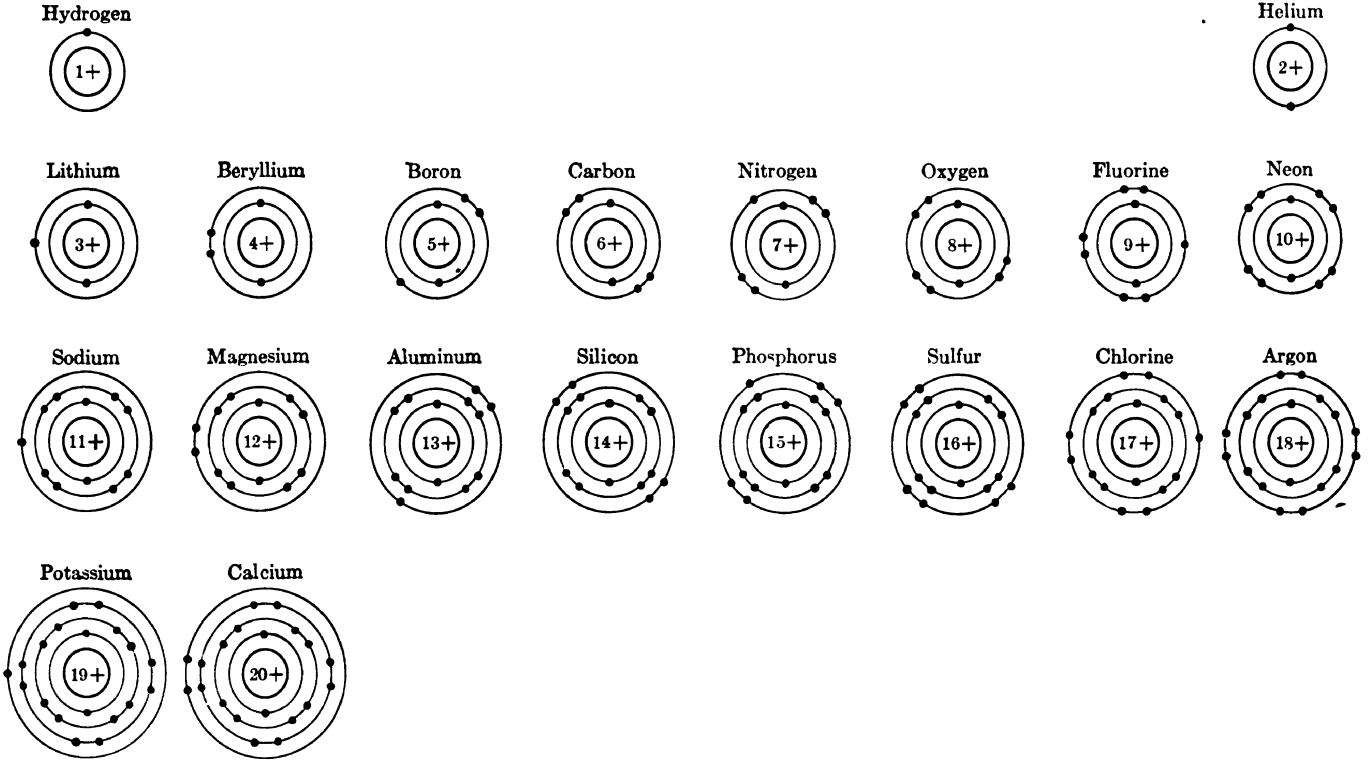


Fig. 4-5. Showing the Positive Charge on the Nucleus for the Atoms of the First Twenty Elements, Hydrogen through Calcium, and the Electrons in the Levels outside the Nucleus

find that in crystals they form clusters of positive and negative ions in ordered piles or in a sort of checkerboard pattern like that shown in Fig. 4-6. There it will be noted that each positively charged ion is surrounded by negatively charged ions; likewise, each negatively charged ion is surrounded by positively charged ions. Compounds made up of ions are called *electrovalent* compounds, and the attractive forces that bind the ions together in crystals are called electrovalent bonds.

Of course many billions of ions are involved in the formation of even a tiny crystal of the compound. When chemists write the formula for sodium chloride as NaCl, they are not expressing a molecule of sodium chloride, but rather the ratio in which the ions are present, 1 to 1.

The 1-to-1 ratio is required for sodium chloride in order to give an electrically neutral combination of ions. Likewise, for calcium ions, Ca^{++}, and chlorine ions, Cl^-, experiment shows a ratio of Ca^{++} to $2Cl^-$, and we write the formula $CaCl_2$. For aluminum ions, Al^{+++}, and chlorine ions, Cl^-, the formula is written $AlCl_3$. In both cases the ratio of the ions is such as to form an electrically neutral compound.

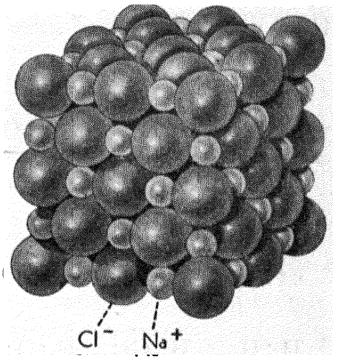


Fig. 4-6. Arrangement of Ions in a Crystal of Sodium Chloride

Some Atoms React by Sharing Pairs of Electrons · Let us consider the reaction of hydrogen with oxygen to form water as an illustration of another way in which atoms may react. Each hydrogen atom has one electron in its outer shell; an oxygen atom has six electrons (Fig. 4-5). It is not true that the two atoms of hydrogen give over their two electrons entirely to the oxygen atom to complete its shell to eight electrons, and thus form a compound of the type H^+, O^-, H^+ (although some chemists at one time thought that this might be so); rather, the hydrogen atoms *share* their electrons with the oxygen. This may be represented as

$$2H\cdot + :\ddot{O}: \longrightarrow H\cdot\ddot{O}:H$$

We see that the oxygen atom has achieved a stable shell of eight electrons by this sharing process, and the hydrogen atoms have each acquired the stable two-electron configuration of the helium atom.

Covalent Compounds · The combination of two hydrogen atoms with one oxygen atom forms a particle of water which we call a molecule of water. The shared pair of electrons between hydrogen and oxygen forms a strong bond between the atoms; it is called a covalent bond. It seems

likely that these pairs of electrons are circulating around the joined atoms, as in Fig. 4-7, but spend most of their time between the atoms. Compounds made up of atoms bound together with covalent bonds are called covalent compounds.

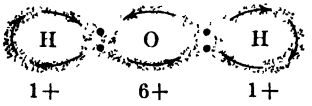
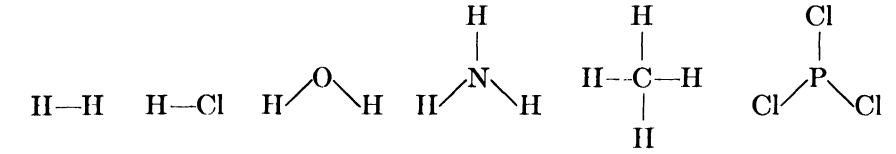
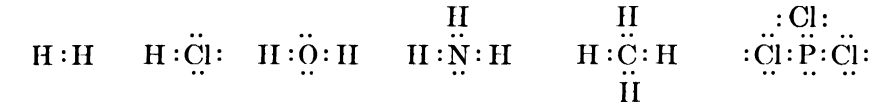


Fig. 4-7. Covalent Bonds

We can represent the covalent bond by a line between the symbols of the joined atoms, H—O—H; and whenever we draw such a line bond, we have in mind to indicate a shared pair of electrons. Furthermore, these bonds are directed in space from the central atom at certain definite angles from each other. The following formulas and models show the structure of some typical molecules of covalent compounds, in which the atoms are tied together in clusters, by covalent bonds, in contrast with the electrovalent compounds, with their ordered piles of ions in definite ratios:



Formula for a molecule of hydrogen | Formula for a molecule of hydrogen chloride | Formula for a molecule of water | Formula for a molecule of ammonia | Formula for a molecule of methane | Formula for a molecule of phosphorus trichloride



These formulas illustrate the formation of completed stable shells of eight electrons (two for hydrogen) by atoms in covalent compounds. Later we shall give a more detailed discussion of electron patterns in molecules.

Crystals of covalent compounds are made up of *molecules* in ordered piles or patterns, just as crystals of electrovalent compounds (Fig. 4-6) are made up of ordered piles or patterns of *ions*.

What Is the Combining Capacity of Atoms? · Why do some atoms combine in the ratio 1 : 1, others in the ratios 1 : 2, 1 : 3, or 2 : 3? We may find the answer to this question if we consider the two ways in which atoms attain stable electron configurations.

1. The combining capacity of atoms that gain or lose electrons is indicated by the number of electrical charges on the ions. For example, Na^+, Ca^{++}, and Al^{+++} ions will combine with 1 Cl^-, 2 Cl^-, and 3 Cl^- ions respectively. Hence we say that the combining capacity of Na^+ is 1, Ca^{++} is 2, Al^{+++} is 3, and Cl^- is 1. This combining capacity of the ions is also called the *electrovalence* of the ions, and may be either positive

or negative. Positive ions combine with negative ions in such a ratio as to form neutral compounds.

2. The combining capacity of atoms that share pairs of electrons is indicated by the number of pairs of electrons shared. For example, hydrogen atoms combine with oxygen atoms to form water molecules:

$$H:\ddot{O}:H$$

Each hydrogen atom shares 1 pair of electrons; hence its combining capacity, or covalence, is 1. Each oxygen atom shares 2 pairs of electrons; we say that its combining capacity, or covalence, is 2.

Summary · Atoms are not only small in size but also small in weight. The relative weights of atoms of different elements are called atomic weights.

Atoms consist of positively charged nuclei made up of protons and neutrons, and of electrons occupying shells around the nuclei.

Atoms react with each other by gaining or losing electrons to form electrovalent compounds, or by sharing pairs of electrons to form covalent compounds. In each case stable electron configurations like those of the inert gases are attained.

QUESTIONS

1. Give a precise definition of (*a*) an element, in terms of atoms and atomic number; (*b*) molecule of a compound; (*c*) molecule of an element; (*d*) ion; (*e*) electron; (*f*) proton; (*g*) neutron; (*h*) atomic number of an element; (*i*) chemical symbol; (*j*) chemical formula; (*k*) electrovalent compound; and (*l*) covalent compound.

2. Give the names and symbols of ten common elements; the formulas of three common compounds.

3. Which of the following are symbols of elements? Which are formulas of compounds? In the latter case, what are the elements of which the compounds are composed? (*a*) P; (*b*) Ca; (*c*) CO; (*d*) Pb; (*e*) Co; (*f*) Os; (*g*) HOCl.

4. Draw structural formulas showing arrangement of *valence electrons*, and also structural formulas using lines to represent shared pairs of electrons for each of the following molecules: (*a*) PH_3; (*b*) $SiCl_4$; (*c*) Cl_2; (*d*) HF.

5. What are the ions in each of the following electrovalent compounds? (*a*) NaF; (*b*) $CaCl_2$; (*c*) Al_2O_3; (*d*) K_2S.

6. What would you expect the formula to be of the electrovalent compound formed when aluminum (Al) reacts with fluorine (F)? with sulfur (S)? Consult Fig. 4-5 for valence electrons.

PROBLEMS

1. If an oxygen atom is 16 times as heavy as a hydrogen atom, calculate the per cent of oxygen and of hydrogen in water, whose formula is H_2O.

2. If 6.02×10^{23} molecules of water occupy 18 ml, how many water molecules will be in a glass full of water if the volume of the glass is 350 ml?

3. What per cent of the weight of an atom of sodium (Na) is made up of electrons?

CHAPTER 5

OXYGEN

Historical · Since we live at the bottom of a great sea of gases, about one fifth of which is oxygen, one might naturally suppose that this element would have been one of the first to be obtained in an approximately pure state and to be recognized as elementary in character. But the separation of a pure gas from the mixture that constitutes air was a task far beyond the ability of the early chemists. The first ones to get oxygen in anything like a pure condition did not get it from air, but from certain of its compounds.

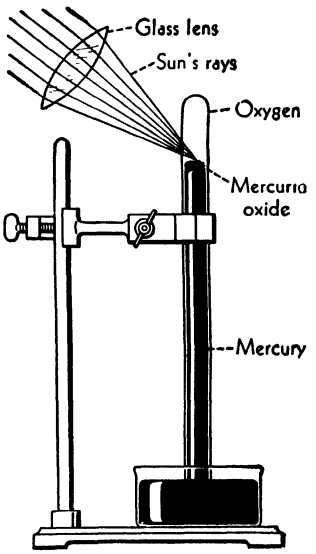


Fig. 5-1. Diagram of Apparatus to Illustrate Priestley's Method of Preparing Oxygen

Credit for the discovery of oxygen is given jointly to Joseph Priestley (Fig. 5-2), an English clergyman and investigator, and Scheele (Fig. 15-1), a Swedish chemist. Although Scheele actually prepared the gas a year earlier than Priestley, the major credit is given to the latter because he was the first to publish his results and describe the properties of the gas.

Priestley's discovery was made in 1774. In the course of some experiments with gases, or "airs" as he called them, it occurred to him to try the effect of heat upon certain solids in order to find out whether any gas is liberated by this means, and, if so, to collect the gas and to study its properties. Accordingly he floated the solids on mercury contained in a tube inverted over mercury, and heated them by focusing the sun's rays upon them by means of a large glass lens (Fig. 5-1). Among the solids so heated was the compound *mercuric oxide.* Collecting some of the gas which was given off, Priestley was surprised to find that a candle burned in it with a remarkably brilliant flame.

At the time of Priestley's discovery the renowned French chemist Lavoisier (Fig. 5-3) was engaged in a study of the mystery of "burning," and at once he became greatly interested in this newly discovered gas. He found that a number of elements such as phosphorus and sulfur burn

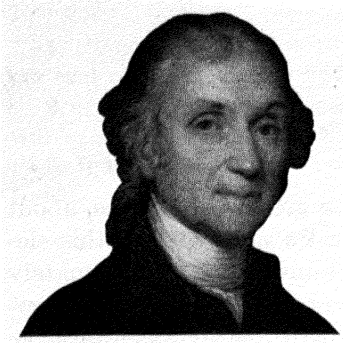


Fig. 5-2. Joseph Priestley (1733–1804) · Distinguished English schoolteacher, philosopher, preacher, and scientist The treatment he received because of his liberal political views led to his emigration to the United States in 1794. He settled at Northumberland, Pennsylvania, where he continued his investigations until his death. The house in which he lived is preserved as a memorial to him. He isolated many important gaseous substances, including oxygen, hydrogen chloride, ammonia, carbon monoxide, nitric oxide, nitrous oxide, sulfur dioxide, and hydrogen sulfide

in it to form compounds which were at that time regarded as acids. Believing that the characteristic properties of acids were due to the presence in them of this substance, he proposed the name *oxygen* for it, a word derived from two Greek words which together give the meaning "acid former." We now know that this name is not entirely appropriate, since many acids do not contain oxygen.

Occurrence · Among all the elements, oxygen easily stands first in order of abundance. It occurs in nature both in the free state and as a constituent of many compounds. In 100 volumes of dry air there are approximately 21 volumes of the free element. In the combined state it constitutes 88.81 per cent by weight of water and nearly one half by weight of the common minerals, such as limestone, sandstone, granite, and clay, which together make up the earth's crust. It is also an essential constituent of the compounds present in living organisms. For example, nearly two thirds of the human body is oxygen. The total weight of oxygen in the land, in the water, in the atmosphere, and in living organisms is roughly equal to the weights of all the other elements taken together.



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Fig. 5-3. Antoine Laurent Lavoisier (1743–1794) Distinguished French chemist, one of the greatest of all time. He demonstrated the true nature of combustion; introduced system into the naming and grouping of chemical substances; showed that bases and acids unite to form salts; filled important positions in the French government; and was guillotined during the French Revolution because of his connection with the former government

Preparation · Since oxygen is so abundant and is present in such a great variety of compounds, it is easy to understand why many different methods may be used to obtain it in pure condition. The most important of these are the following:

1. **Preparation by heating certain compounds of oxygen.** Many compounds containing oxygen give off at least a portion of it when heated. For example, mercuric oxide (HgO) and potassium chlorate ($KClO_3$)—compounds which contain, respectively, 7.4 per cent and 39.2 per cent of oxygen—give off all their oxygen when heated to a moderately high temperature. Other compounds, such as sodium nitrate and barium peroxide, give up only a portion of their oxygen.

The heating of an oxygen compound is a convenient method for preparing the small quantities of oxygen needed in the laboratory. The compound usually chosen is the colorless solid potassium chlorate, whose formula is $KClO_3$. The evolution of the gas becomes marked at about 400°; and if the heating is continued long enough, all the oxygen present in the potassium chlorate is liberated. It is a remarkable fact that the rate at which the oxygen is evolved at any given temperature is greatly increased by the presence of small quantities of certain substances, notably manganese dioxide. By mixing some manganese dioxide with the chlorate it is possible to liberate the oxygen rapidly at a much lower temperature, namely, at about 200°.

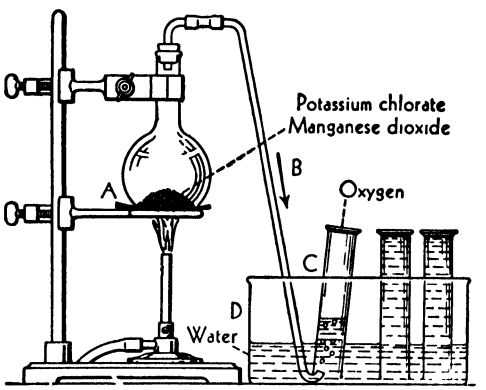


Fig. 5-4. Diagram of Apparatus for Preparing Oxygen from Potassium Chlorate

Details of Laboratory Method · The operation, as carried out in the laboratory, is as follows: The potassium chlorate, mixed with about one fourth of its weight of manganese dioxide, is placed in a suitable vessel, such as a glass flask, which is provided with a stopper and glass tube, as shown at *A* (Fig. 5-4). On heating the mixture gently, oxygen is evolved and passes out through the tube, *B*. It is evident that the oxygen at first escaping is mixed with the air contained in the flask. In a short time, as the evolution of oxygen continues, all this air is displaced, and the pure oxygen may then be collected by bringing the end of the delivery tube under the mouth of a glass cylinder, *C*, which has been filled with water and inverted in a trough of water, *D*, as shown in the figure. The gas rises in the cylinder and displaces the water.

Characteristics of Potassium Chlorate · The composition (by weight) of potassium chlorate ($KClO_3$) has been found to be as follows: potas-

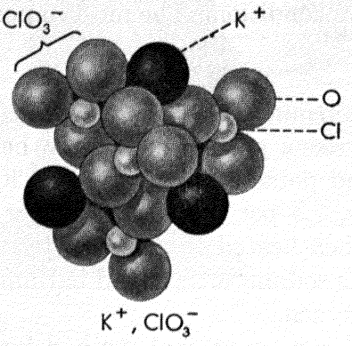


Fig. 5-5. Showing the Potassium Ions and Chlorate Ions in a Tiny Fragment of a Potassium Chlorate Crystal

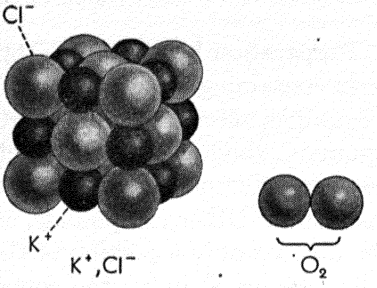


Fig. 5-6. Showing the Potassium Ions and the Chloride Ions in a Tiny Fragment of a Crysta of Potassium Chloride; Showing Also an Oxygen Molecule

sium, 31.9 per cent; chlorine, 28.9 per cent; oxygen, 39.2 per cent. When the substance is heated, changes occur which finally result in the liberation of all the oxygen, while the potassium and chlorine remain in the form of a colorless solid compound known as potassium chloride (KCl). The experimental fact that potassium chlorate yields potassium chloride and oxygen when heated is recorded in the chemical equation

$$\underset{\text{potassium chlorate}}{2\,KClO_3} \longrightarrow \underset{\text{potassium chloride}}{2\,KCl} + \underset{\text{oxygen}}{3\,O_2}$$

Catalysts · We do not know the mechanism by which manganese dioxide increases the rate of decomposition of potassium chlorate so that oxygen is given off rapidly at a relatively low temperature. Apparently the manganese dioxide undergoes no permanent change during the reaction. Certainly it contributes no oxygen, for the weight of the oxygen obtained is always 39.2 per cent of the weight of the potassium chlorate used, irrespective of the presence of manganese dioxide. This is but one example of many in which the rate of a chemical change is influenced by a foreign substance. Such a substance is called a *catalyst* or a *catalytic agent*; it may be defined as *a substance which alters the speed of a chemical reaction without itself being permanently changed.*

It is true that manganese dioxide gives up some of its oxygen when heated; but this requires a temperature above 400°, while the temperature reached in the preparation of oxygen from a mixture of potassium chlorate and manganese dioxide is only about 200°.

2. **Preparation from sodium peroxide.** A more convenient, although more expensive, method for preparing oxygen in the laboratory consists in adding water to sodium peroxide. These two compounds, when brought into contact with each other, react in such a way as to liberate oxygen (Fig. 5-7). At the same time a colorless solid compound is formed, consisting of sodium, hydrogen, and oxygen, known as sodium hydroxide:

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

sodium peroxide — water — sodium hydroxide — oxygen

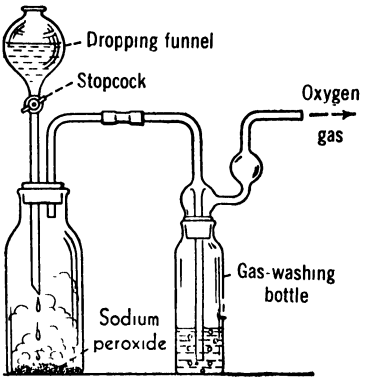


Fig. 5-7. Diagram of Apparatus Used for Preparing Oxygen by the Action of Water on Sodium Peroxide

3. **Preparation by the electrolysis of water.** The compound water contains 88.81 per cent by weight of oxygen and 11.19 per cent by weight of hydrogen. If a small amount of sulfuric acid or sodium hydroxide is dissolved in the water to make it a good conductor of electricity, it is easily decomposed into its elements by passing through it an electric current from a battery (Fig. 3-1, p. 22):

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

This method is useful in the laboratory and is also used to some extent on a commercial scale.

4. **Preparation by the fractional distillation of liquid air.** Since air contains such a large percentage of free oxygen, one would naturally expect methods to be devised for obtaining it from this source. The problem is not as simple as it may seem, for there are other gases in the air, and the separation of a gas in a pure condition from a mixture of gases is generally difficult. In this case it may be accomplished by a purely physical method, as follows:

By subjecting air to the combined effects of high pressure and very low temperature it is possible to obtain it in the form of a liquid, which is essentially a mixture of liquid oxygen and liquid nitrogen. If this mixture of liquids is allowed to stand at ordinary pressures, the nitrogen rapidly boils away, since it has a lower boiling point than oxygen, and the oxygen is left as a relatively pure liquid. The separation of liquids by taking advantage of their difference in boiling points in this way is called *fractional distillation.* The oxygen may be transported as a liquid in gigantic Dewar flasks ("Thermos bottles") or may be allowed to change to a gas and be pumped into strong steel cylinders under a

high pressure. In the United States at the present time nearly all the oxygen prepared for commercial purposes is obtained from liquid air, since this is the cheapest method of preparation on a large scale.

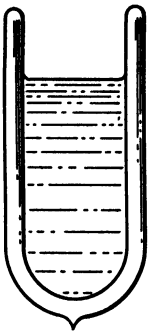


Fig. 5-8. The Dewar Flask · Such flasks are made in many forms, of which the Thermos bottle is one. The double walls are silvered on the inside to reduce loss of heat by radiation. The space between the walls is pumped out to a good vacuum to reduce conduction of heat. Such a vessel is excellent for storing low-boiling liquids. The flask was invented by Sir James Dewar, about 1892

Physical Properties · Oxygen is a colorless, odorless, and tasteless gas. At 0° and under a pressure of 1 atmosphere (atm) 100 ml of water dissolves 4.96 ml of the gas; thus it is not very soluble, and may be collected over water with but little loss. One liter of oxygen, measured at 0° and under a pressure of 760 mm, weighs 1.4290 g. Since 1 liter of air under the same conditions weighs 1.2930 g, it will be seen that oxygen is 1.105 times as heavy as air.

To accomplish the liquefaction of oxygen, the temperature must be at least as low as − 118.8°, at which temperature a pressure of 49.7 atm is required (see critical temperature, Chap. 11). At still lower temperatures less pressure will suffice. Liquid oxygen has a slightly bluish color and boils at − 183° under a pressure of 1 atm. At its boiling point the liquid has a density of 1.14. By cooling this liquid to an extremely low temperature Dewar, an English investigator, succeeded in freezing it to a snowlike solid which melts at − 218.4°.

Two Atoms in the Oxygen Molecule · In the foregoing equations we have represented oxygen not by its symbol alone, O, but by O_2. This indicates that a molecule of oxygen gas contains two atoms; it is a *diatomic* molecule. Most of the common elementary gases have diatomic molecules; thus, the hydrogen, nitrogen, and chlorine molecules have the formulas H_2, N_2, and Cl_2. Other substances form monatomic gases, as gaseous mercury (Hg) and neon (Ne). On the other hand, elementary gases with more than two atoms are known; phosphorus and arsenic have the formulas P_4 and As_4 in the gaseous state, and oxygen also forms triatomic molecules (O_3) under certain conditions (see ozone).

Chemical Properties · At ordinary temperatures oxygen is only a moderately active element– a fact which may be inferred from our experience

that very few of the materials coming under common observation are acted upon by the oxygen of the air with noticeable rapidity. With rise in temperature it rapidly becomes more active. At ordinary temperatures, for example, the elements sulfur, iron, and carbon are not visibly acted upon by oxygen, while in the case of phosphorus the action, though apparent, is quite slow. If now the temperature of each of these elements is slowly raised, the reaction becomes more marked, and the phosphorus soon bursts into flame. At higher temperature the sulfur, carbon, and iron are likewise ignited. If each of these elements, as soon as ignited in the air, is introduced into a vessel of pure oxygen (Fig. 5-9), the action becomes much more energetic. The pale-blue flame of the burning sulfur is greatly increased in size and brightness, the iron throws off countless sparks, while the phosphorus and carbon burn with dazzling brilliancy. In each case the action increases in intensity as it progresses. Many compounds act in the same general way. Thus wood, coal, oil, fats, and fuel gases all burn readily in air and more brilliantly in pure oxygen. It was a brilliant candle flame that led Priestley to the discovery of oxygen (p. 45). Indeed, there are but few, if any, elements which will act upon so many other elements and compounds as does oxygen.

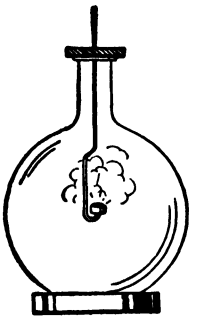


Fig. 5-9. Burning Sulfur in Oxygen

This general conduct suggests a great many questions. What becomes of the substances when they burn? Why do not all substances burn? Why does the action become more energetic and brilliant as it progresses? Why is there a difference in the case of ignition? Why do substances burn better in oxygen than in air? These questions may be answered in part at once; similar questions will occur many times in our study, and in the end will remain only partially answered.

Products of Oxidation: Oxides · Experiments have shown that the action of oxygen upon another element consists in the union of the two elements to form a compound. Thus the reactions of the burning of several elements may be represented by the following equations:

$$2\,Mg + O_2 \longrightarrow 2\,MgO \text{ (magnesium oxide)}$$
$$4\,Al + 3\,O_2 \longrightarrow 2\,Al_2O_3 \text{ (aluminum oxide)}$$
$$P_4 + 5\,O_2 \longrightarrow P_4O_{10} \text{ (phosphoric oxide)}$$
$$S + O_2 \longrightarrow SO_2 \text{ (sulfur dioxide)}$$
$$C + O_2 \longrightarrow CO_2 \text{ (carbon dioxide)}$$

The action of oxygen upon compounds is similar to its action upon elements, and usually consists in the union of oxygen with one or more of

the elements present in the compound. Thus, when the compound methane (CH_4) burns, both the carbon and the hydrogen combine with the oxygen:

$$\underset{\text{(1 molecule)}}{CH_4} + \underset{\text{(2 molecules)}}{2\,O_2} \longrightarrow \underset{\text{(1 molecule)}}{CO_2} + \underset{\text{(2 molecules)}}{2\,H_2O}$$

The presence of water in the products of this reaction is shown by the momentary condensation of water on the outside of a cold pan when it is set over the flame of a gas stove. (Methane is the chief constituent of natural gas.) In some cases the compound as a whole unites with the oxygen:

$$\underset{\text{lead sulfide}}{PbS} + 2\,O_2 \longrightarrow \underset{\text{lead sulfate}}{PbSO_4}$$

A substance which undergoes combination with oxygen is said to be *oxidized*, and the process or change which takes place is called *oxidation*. Thus, we say that phosphorus is readily *oxidized* or that it easily undergoes oxidation. Oxidation may be brought about by the use of oxygen or of some compound that will readily supply oxygen, such as potassium chlorate or sodium peroxide. When so used, the oxygen itself or the compound which furnishes the oxygen is called the *oxidizing agent*.

It will be pointed out in the appropriate place that the use of the term *oxidation* is not limited to such changes as those mentioned above but has a much broader application, embracing a large group of reactions, in many of which no oxygen takes part. For the present, however, the term will be used in the sense explained above.

When any element combines with oxygen, the resulting compound is known as an *oxide* of that element, as indicated by the parenthetical names in the equations given at the bottom of page 51. *An oxide is any compound composed of two elements, one of which is oxygen.* The particular oxides formed in the oxidation of any substance are known in general as the *products of oxidation* of that substance.

With the exception of the rare gases, all the elements form stable oxides; indeed, some of the elements form more than one oxide, as is the case with carbon, which forms carbon monoxide (CO) and carbon dioxide (CO_2). Some of the oxides are invisible gases, as is true of the oxides of sulfur and carbon, formed when these two elements burn in air or in pure oxygen. In a few cases the oxide is a liquid, the most familiar example being water, which is an oxide of hydrogen. In the great majority of cases, however, the oxides are solids.

Oxides of Metals and Oxides of Nonmetals · From the chemical standpoint oxides are divided into two great classes, of distinctly different

properties and behavior: the *oxides of metals*, such as those of iron, magnesium, and aluminum, and the *oxides of nonmetals*, such as those of carbon, phosphorus, and silicon.

Of the several properties which distinguish the two great classes of oxides from each other, the most striking is their reaction with water. A metallic oxide unites chemically with water to form a compound that we call a *base*. Bases are identified, or tested for, by their characteristic action in changing the color of the vegetable dye *litmus* from red to blue. A nonmetallic oxide unites with water to form a compound that we call an *acid*. Acids turn blue litmus to red. Some of the oxides react with water vigorously, others very slowly. Some of the acids and bases thus produced are soluble in water; others are extremely insoluble.

Equations for the reactions of some oxides with water to form acids and bases are as follows:

Acids:

$$SO_2 + H_2O \longrightarrow H_2SO_3 \text{ (sulfurous acid)}$$

$$CO_2 + H_2O \longrightarrow H_2CO_3 \text{ (carbonic acid)}$$

$$SiO_2 + 2\,H_2O \longrightarrow H_4SiO_4 \text{ (silicic acid)}$$

(Silicic acid forms and goes into solution readily only in superheated water.)

Bases:

$$Na_2O + H_2O \longrightarrow 2\,NaOH \text{ (sodium hydroxide)}$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \text{ (calcium hydroxide)}$$

$$MgO + H_2O \longrightarrow Mg(OH)_2 \text{ (magnesium hydroxide)}$$

$$Al_2O_3 + 3\,H_2O \longrightarrow 2\,Al(OH)_3 \text{ (aluminum hydroxide)}$$

The molecules of an acid are characterized by the presence of hydrogen atoms, as in sulfurous acid (H_2SO_3). In water solution an acid molecule furnishes hydrogen ions (H^+):

$$H_2SO_3 \longrightarrow 2\,H^+ + SO_3^{--}$$

In much the same way the molecules of a base are characterized by the presence of hydroxyl groups (OH), as in NaOH; and in water solution a molecule of a base yields hydroxyl ions (OH^-):

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

Weight Relations in Oxidation · Since oxidation is essentially the union of oxygen with other elements or compounds, it must follow that the weight of the product formed is greater than that of the substance oxidized or burned. Our common experience with fuels would hardly lead us to such a conclusion, because the ash remaining after burning represents only a small fraction of the total weight of fuel consumed. But, of course, the products of ordinary combustion, largely water and oxides of carbon, are volatile and escape up the chimney. Experiments

may be performed in which these gaseous products are collected and weighed. Here, as in all other cases, it can be shown that the weight of the substance oxidized, plus that of the oxygen used up, exactly equals the weight of the products of the oxidation.

Incombustible Substances · The question naturally arises, Why do not all substances burn? In the case of many substances, such as the compounds formed in combustion, the answer is very evident, for they already contain all the oxygen with which they are capable of uniting. Many oxides, such as water, are of this class, as well as most of the substances which constitute the solid crust of the earth. The materials of which fireproof buildings are made—brick, tile, cement, plaster, asbestos—are also of this character. Some of the metals, like iron, will burn, but only at high temperatures; otherwise they are practically incombustible unless they are in a finely powdered form. Other substances, however, such as the elements helium and argon, do not combine with oxygen under any known conditions.

Heat, Temperature, and Light in Oxidation; Combustion · In the oxidation of the elements that we have been considering, the rate of oxidation may at first be quite slow, with little heat given out and no light. If the conditions are such that the loss of heat by radiation and conduction is small, the major portion of the accumulating heat serves to raise the temperature of the materials involved in the reaction. The higher the temperature, the faster the reaction proceeds. As the oxidation continues, therefore, heat is given off at an increasingly rapid rate, which raises the temperature still farther. Light may appear, in some cases becoming almost blinding. The higher the temperature, the larger is the fraction of heat converted into visible radiant energy (light). Increasing brightness is therefore an indication of rising temperature.

Such a reaction is called a *combustion*. Although this term is often used as a synonym for *oxidation*, it is usually reserved for those chemical reactions which are accompanied by the evolution of heat *and light*. The most familiar examples of combustion are those in which substances "burn" in air or oxygen, but in subsequent pages we shall meet with cases of combustion in which no oxygen takes part in the reaction.

Ease of Ignition; Kindling Temperature; Spontaneous Combustion · Before any substance will undergo self-sustaining combustion,—that is, before it will ignite,—its temperature must be raised to a definite point known as its *kindling temperature*. This temperature varies from substance to substance and also with the reaction conditions for the same substance. Thus, the kindling temperature of phosphorus is very low, while that of iron is much higher.

Materials taking fire on their own account, without the application of a flame or spark, are said to undergo *spontaneous combustion.* It will be seen that the essential conditions are (1) an existing slow oxidation and (2) good heat insulation.

Illustrations · Linseed oil, used in paints, may attain rather rapid oxidation in air, and oily rags left by painters not infrequently occasion disastrous fires. Fine coal in the center of a heap or in the closed hold of a vessel sometimes takes fire. Almost any finely divided combustible material, such as sawdust or flour, is dangerous when stored in a warm, dry place. Sometimes the heat of rotting or of fermentation will start a fire in a haystack or a barn if the hay is not well dried before being stored

Rate of Chemical Reactions · The description of the conditions which lead to spontaneous combustion, and also the description of the course of the decomposition of potassium chlorate, have made it clear that a given chemical reaction may take place at different rates under different conditions. We recognize five important factors which control the rate of chemical reactions in general.

1. The *nature* of the reacting substances is of prime importance.

2. Once we have chosen the reacting substances for a given reaction, it is true that the *temperature* is extremely important; the higher the temperature, the faster the reaction.

3. Increasing the *concentration* of the reacting substances causes the reaction to increase in rate. By the "concentration" of a substance we mean the amount of it in a given volume. One of the reasons why substances burn better in oxygen than in air is that the concentration of oxygen is higher when it is pure than when it is present as a component of air. Thus, a one-liter vessel filled with oxygen at 0° and under a pressure of 760 mm would contain 1.429 g of oxygen; the same vessel filled with air under the same conditions would contain only 0.300 g of oxygen.

4. In a reaction between a solid and a liquid or a gas the rate of the reaction is increased by increasing the *amount of surface* exposed to attack (for example, the surface may be enlarged by increasing the degree of subdivision).

5. The presence of a *catalyst* modifies the rate profoundly.

All these factors will be treated in detail in Chapter 24.

Importance of Oxygen · The great importance of oxygen in nature is evident from the facts which have already been presented in this chapter. It is a constituent of the great majority of the compounds which collectively constitute the solid earth, the living creatures upon it, and the

water which covers so much of its surface, while the atmosphere is a great reservoir from which a supply of the free element can be drawn at any time.

Free oxygen is essential to the life of all organisms, with the exception of some of the lowest microscopic forms. Aquatic animals obtain the necessary oxygen from the air dissolved in the water in which they live. In animals the oxygen inhaled into the lungs is absorbed by the blood and carried throughout the body; it enters into the cells composing the tissues, and oxidizes old tissues and food materials. These oxidations serve to maintain the temperature of the body. The major oxidation products, carbon dioxide and water, are brought back to the lungs by the venous blood and expelled on exhaling.

It is interesting to note that human beings cannot live for long in air in which the concentration of oxygen has been reduced to about one half of the normal amount present in a liter at sea level. It is about 0.3 g of oxygen. For this reason aviators are supplied with oxygen for use at high altitudes; at eighteen thousand feet only about one half as much air, and consequently only about one half as much oxygen, is contained in a given volume as at the surface of the earth. Nor will a candle burn, or other usually combustible material, if the concentration of oxygen in air is in the range of one half to one fourth of the normal amount. On the other hand, a relatively small increase in the concentration of oxygen in the atmosphere would greatly increase the rate of burning; and fires of all sorts would become practically inextinguishable.

Free oxygen also plays a prominent part in the decomposition of refuse matter which collects on the surface of the earth, much of it being oxidized into harmless gases. Sewage is sometimes purified by spraying it into the air so that oxygen can come in contact with the noxious materials and oxidize them. It is noteworthy, however, that the oxidation of such matter takes place only in the presence of certain forms of minute living organisms known as *bacteria*.

Commercial Uses of Oxygen · Enormous quantities of oxygen from 95 to 100 per cent pure are now prepared from liquid air for commercial uses. By far the greater part of commercial oxygen is used in the production of high temperatures for the cutting and welding of metals (see oxyacetylene blowtorch, Chap. 33) and for enriching the air used in blast furnaces for the production of iron, and as a reagent in various industrial chemical processes. Smaller amounts are used for the treatment of those diseases (such as pneumonia) in which the patient is unable to inhale sufficient air to supply the necessary quantities of oxygen. Miners inhale oxygen, from an oxygen-tank respirator, when entering mines after an

explosion. Pure oxygen may be inhaled for a number of hours, apparently without injurious effects.

Ozone

In addition to the common diatomic molecule O_2, oxygen also forms a molecule with the formula O_3. This substance is called *ozone* (from a Greek word meaning "to smell") because of its peculiar characteristic odor.

Preparation · Ozone is formed when an electric spark is passed through oxygen, or when oxygen is passed between plates that are highly charged electrically (which gives the so-called silent discharge); in this way the heating effect of a spark discharge is avoided (Fig. 5-10).

To obtain the greatest yield the oxygen should be cold and free from moisture. Under ordinary conditions 5–10 per cent of the oxygen is converted into ozone. At lower temperatures a larger yield may be obtained, reaching 90 per cent at the temperature of liquid air. To prepare pure ozone the mixture of oxygen and ozone is cooled with liquid air. The ozone, being much more readily condensed than oxygen, is obtained in a liquid state almost free from oxygen.

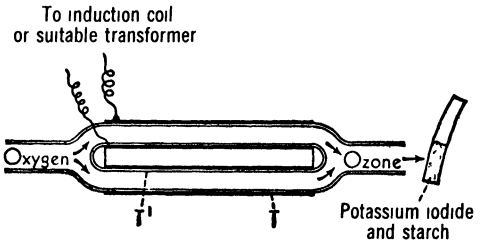


Fig. 5-10. Diagram of Apparatus Used for Preparing Ozone by the Action of the Electric Discharge on Oxygen

Ozone is formed in small percentages in reactions in which oxygen is liberated at low temperatures, as in the decomposition of water by the electric current. It is also produced in some oxidations, as when moist phosphorus slowly oxidizes in air.

Properties · Ozone is a gas of pale-blue color and characteristic odor. It is 1.5 times as heavy as oxygen, since 1 liter of the gas weighs 2.144 g. When cooled sufficiently, it condenses to an indigo-blue liquid which boils at −112°.

Ozone resembles oxygen in its chemical properties but is much more active and is therefore a very powerful oxidizing agent. Such metals as silver and mercury, which are not easily acted upon by oxygen, quickly tarnish in air containing ozone. It reacts with potassium iodide to liberate iodine. This reaction is used as a test for the presence of ozone by allowing the gas to come in contact with paper which has been dipped into a solution of potassium iodide and starch; the iodine formed by the ozone

reacts with the starch to give a blue color. Ozone also oxidizes many organic dyes, forming colorless compounds, and so acts as a bleaching agent; and in concentrations of about 15 parts per 100 million of air will cause a noticeable increase in the rate of deterioration of rubber tires. When pure, it is a dangerous explosive, owing to its spontaneous conversion into oxygen.

In view of its great activity it is doubtful whether ozone is ever present in the air near the earth's surface in appreciable quantities. It is doubtless formed during lightning discharge, but it must very speedily disappear through chemical action upon oxidizable materials like pollen grains and other fine organic dusts, which are always floating through the air. The air collected on high mountaintops, however, is said to contain recognizable percentages of ozone; and it is formed in the upper regions of the atmosphere by the action of the ultraviolet light from sunshine. The ozone then strongly absorbs the ultraviolet rays and greatly reduces the intensity of the rays that penetrate to the bottom of the atmosphere. By this absorption the ozone makes the existence of life on the earth possible, because exposure to ultraviolet light of appreciable intensity is soon deadly to both plants and animals.

Uses of Ozone · Ozone has certain commercial applications, all based on its strong oxidizing properties. Thus, it is used as a bleaching agent, as a disinfectant, as a deodorizer, and as an oxidizing agent in the preparation of a number of useful products. It is also being used in Europe for the sterilization of drinking waters. The substance employed for these various purposes is not pure ozone but ozonized air, which is prepared as it is needed. Ozone at a concentration of about 2 parts per million of air is very damaging to lung and other tissues after an exposure of several hours.

The Conversion of Oxygen into Ozone Reversible · The reason why only a relatively small percentage of the oxygen subjected to an electric discharge is transformed into ozone is that under all ordinary conditions ozone changes back into oxygen. These two opposite changes may be represented as follows, the arrows indicating the direction in which each change proceeds:

$$\underset{\text{oxygen}}{3\ O_2} \rightleftarrows \underset{\text{ozone}}{2\ O_3}$$

When the speed with which the oxygen changes into ozone exactly equals the speed with which the resulting ozone changes back into oxygen, the two substances are said to be in a *state of equilibrium.* The percentage of ozone present when equilibrium is reached is clearly the maximum yield under the conditions of the experiment. Such reactions as the above are termed *reversible reactions.*

The Difference between Oxygen and Ozone · Ozone differs from oxygen not only in the composition of its molecules, but also in its energy content. In the transformation of oxygen into ozone by the usual method electrical energy is absorbed. When ozone spontaneously changes into oxygen, about 717 cal of heat is liberated for each gram so changed; and when it acts as an oxidizing agent, the heat evolved is correspondingly greater than when the same oxidation is accomplished by oxygen.

QUESTIONS

1. Define (*a*) *oxide;* (*b*) *oxidation;* (*c*) *catalyst;* (*d*) *combustion;* (*e*) *diatomic molecule;* (*f*) *speed of reaction;* (*g*) *kindling temperature;* (*h*) *acid;* (*i*) *base.*

2. Air costs nothing and water very little, and both are possible sources of free oxygen. Why is commercial oxygen made from air rather than from water?

3. Both potassium chlorate and manganese dioxide contain oxygen. When a mixture of the two is heated, oxygen is evolved. How would you prove whether the oxygen comes from the chlorate, from the dioxide, or from both?

4. Do we add manganese dioxide to potassium chlorate (*a*) to obtain more oxygen, (*b*) to set free the oxygen at a lower temperature, or (*c*) to set free the oxygen more rapidly at a given temperature?

5. Why does pouring water on a burning building check the speed of the fire?

6. Charcoal burns in air and mercuric oxide decomposes when heated. Write the equation for each of these reactions.

7. Why should ozone (O_3) be a stronger oxidizing agent than oxygen (O_2)?

8. Explain the fact that a small flame can be extinguished by covering it with a blanket.

9. Of what importance is it that the air is only one-fifth oxygen and not all oxygen?

10. Why do we use one method for preparing oxygen in the laboratory and another method for commercial preparation?

11. Does the preparation of oxygen from air involve a physical or a chemical change? Give the reason for your answer.

12. (*a*) Write the equations for two reactions in which acids are formed from oxides and water. (*b*) Write the equations for two reactions in which bases are formed from oxides and water.

PROBLEMS

1. (*a*) If 12 g of carbon reacts completely with 32 g of oxygen to form carbon dioxide (CO_2), what is the weight of carbon dioxide that is formed? (*b*) What per cent of this weight is carbon? (*c*) What per cent is oxygen?

2. Mercuric oxide, potassium chlorate, and water contain respectively 7.4, 39.2, and 88.81 per cent of oxygen by weight. What weight of oxygen can be obtained from 10 g of each one of these compounds?

3. What weight of each of the three compounds in Problem 2 would yield 100 liters of oxygen?

4. In the preparation of oxygen by heating a mixture of 10 g of potassium chlorate and 4 g of manganese dioxide, (*a*) what volume of oxygen would be obtained? (*b*) What compounds would remain in the flask? (*c*) What would be the weight of each of these?

5. Commercially pure potassium chlorate costs about 60 cents per kilogram, and mercuric oxide $4.50 per kilogram. What volume of oxygen could you obtain from one dollar's worth of each of these compounds?

CHAPTER 6

GASES AND THE GAS LAWS; THE KINETIC-MOLECULAR THEORY

The Importance of Studying Gases · It is very important that a chemist understand the behavior of gases under various conditions of collection and storage. In particular, it is important that he understand how the volume of a gas is affected by changes in temperature and pressure. (1) In the first place, chemists must handle gases constantly in the laboratory; and chemical engineers deal with gases in many industrial operations, pumping them from one container to another and through various sorts of reaction vessels. (2) Furthermore, when we are concerned with the quantity of a gas, it is far more convenient to measure the volume of the gas than it is to weigh the gas. (3) Also, several of the fundamental principles of chemical science have developed directly out of a study of gases, as we shall see in this present chapter.

Let us bear in mind also that gases, like all matter, are made up of particles, and that *we set up our explanations of the behavior of matter, in all its many aspects, in terms of the weight, size, shape, and structure of these particles, and in terms of their motions, their mutual attractions and repulsions, and their collisions and combinations with one another.*

Definition of a Gas · A *gas* or *vapor* may be regarded as matter in such a state that it distributes itself uniformly throughout the space or volume in which it is confined. (A *liquid* does not so distribute itself; it has a volume of its own but no characteristic shape, and in so far as it fills a vessel it takes the latter's shape. A *solid* retains its own shape and volume, irrespective of the size or form of the containing vessel.)

If a given substance exists completely in the gaseous state at *ordinary temperatures and pressures*, we call it a gas; if it is ordinarily a liquid or a solid, but evaporates readily, we refer to the evaporated portion as a *vapor*. Thus, we speak of oxygen *gas*, water *vapor*, and camphor *vapor*.

Characteristics of the Gaseous State · It is very significant that the physical conduct of *all* gases is very largely the same and bears no relationship to the chemical composition of the gases. Consequently the characteristics listed below apply generally to the gaseous state.

1. **Expansibility.** The ability of a gas to distribute itself uniformly throughout a volume may be demonstrated by the following experiment:

The small, thin-walled bulb, *A* (Fig. 6-1), is filled with bromine, sealed, and placed in a glass vessel, *B*, which can be closed and exhausted by a vacuum pump attached at *C*. A glass rod is arranged to slip through a tight-fitting rubber stopper, *D*. When the vessel has been exhausted, the rod is pushed down so as to crush the bulb. Instantly the reddish vapor of bromine fills the vessel.

2. **Diffusion.** If two gases, *A* and *B* (Fig. 6-2), are brought in contact, each will penetrate into the other until an even mixture in both vessels is reached. This process is called *diffusion*, and it resembles expansion into a vacuum. It takes place *slowly*, for each gas presents an obstacle

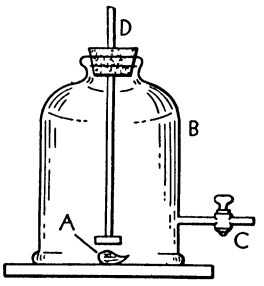


Fig. 6-1. Apparatus Used for Showing the Rapid Expansion of a Vapor in a Vacuum



Fig 6-2 The Diffusion of Gases

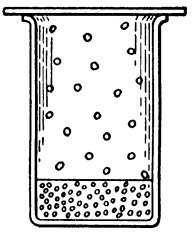


Fig 6-3 Molecules Are Close Together in the Liquid, Dispersed in the Gas

to the expansion of the other. The rates of diffusion are not dependent on gravity, for a heavy gas in *A* will diffuse upward into a lighter one in *B*. Two gases of unequal density, when once mixed, do not separate into layers.

3. **Compressibility.** The differing behavior, toward compression, of liquids and solids, on the one hand, and gases, on the other, reveals one of the important ways in which gases differ from the other states of matter. Liquids and solids offer great resistance to any force tending to squeeze them into smaller volume; they are but slightly compressible. On the other hand, the volume of a gas is greatly altered by comparatively small changes in pressure. A familiar illustration of this is found in the common experience of pumping air into a bicycle or automobile tire. A surprisingly large volume of air may be pumped into what is an almost unchanged volume in the tire.

This contrasting behavior of liquids and gases toward compression is just what we expect when we take into account the nature of liquids and gases. The molecules of a liquid are packed fairly closely together, in contact with one another (Fig. 6-3), and any considerable compression

would have to be a compression of the actual molecules themselves. Molecules resist deformation, and repulsive forces that come into play when molecules are pushed strongly against one another prevent one molecule from invading the domain of another molecule—in other words, prevent two molecules from occupying the same space at the same time.

On the other hand, when a given volume of liquid evaporates, the resulting gas or vapor occupies a volume which is then usually about a thousand times larger, and the molecules are on the average about ten times as far apart as in the liquid state. Such a gas could be compressed by an applied pressure to one half its volume, for instance, and there would still be a great deal of free, empty space through which the gas molecules could move around. Indeed, the gas volume could be compressed right down to the volume occupied by the original liquid, before the resistance to further compression would become appreciable.

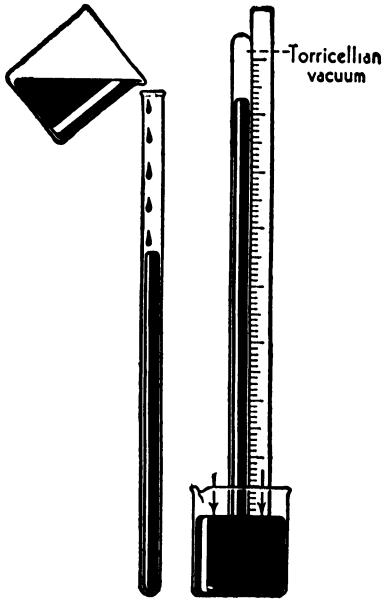


Fig. 6-4. A Simple Type of Barometer Made by Filling a Glass Tube with Mercury and Inverting It in a Well of Mercury

Pressure-measuring Instruments; the Barometer · In the study of gases we obviously must often deal with pressure (as well as temperature). Just as there are several types of instruments used for measuring temperature (pp. 14, 16), so there are many instruments for measuring pressure. One of the simplest is a barometer. A barometer may be constructed by filling a glass tube about 80 cm long (and closed at one end) with mercury, and then inverting it and thrusting the open end into a well of mercury (Fig. 6-4). The mercury column falls until the weight of the mercury in the tube is exactly equal to the weight of a column of air of cross section equal to that of the mercury column and extending from the surface of the mercury in the well to the top of the atmosphere. As the weight of the air changes, owing to changes in the atmospheric pressure, the level of the mercury in the tube moves up or down. The height of the mercury column, read off on a meter stick placed alongside, thus serves as a measure of the atmospheric pressure.

Above the mercury in the tube is a vacuum, called the Torricellian vacuum in honor of the Italian Torricelli, who, while a young student

assistant of Galileo, made the first barometer in very much this way. Incidentally, it is interesting to know that Torricelli's vacuum was the first authentic case of the production of a vacuum. Up to that time, about 1643, it had been supposed that "Nature abhors a vacuum."

Standard Atmosphere · The average barometer reading at sea level is 760 mm. This pressure is known as the standard atmosphere. It is equivalent to 14.7 pounds per square inch (lb/sq in.) or 1033 g/cm^2. In other words, on the average a column of air 1 sq in. in cross section and reaching from sea level to the top of the atmosphere weighs 14.7 lb; a column of mercury 1 sq in. in cross section and 760 mm high weighs the same amount.

The Gas Laws

We shall now consider five laws which serve to describe the conduct of gases under the usual variety of conditions.

1. **Variation of volume with pressure; the law of Boyle.** Recognizing that gases are compressible, suppose we set ourselves the task of

VARIATION OF VOLUME WITH PRESSURE

EXPERIMENT NO.	PRESSURE	VOLUME	PRODUCT, PRESSURE × VOLUME
1	1 atm, P_1	16 ml, V_1	1 × 16
2	2 atm, P_2	8 ml, V_2	2 × 8
3	4 atm, P_3	4 ml, V_3	4 × 4
4	8 atm, P_4	2 ml, V_4	8 × 2
5 . . .	16 atm, P_5	1 ml, V_5	16 × 1

measuring quantitatively how the volume of a gas varies with pressure. We might use an apparatus like that shown in Fig. 6-5. In the shorter and sealed arm of a J-tube, a sample of gas is confined over liquid mercury. Adjusting the mercury level so that it is the same in both arms of the tube (the gas will now be at atmospheric pressure), we read the volume of the confined gas and find it to be 16 ml (Experiment 1 in the table above). Now let us add mercury to the open arm until the level in this arm is higher than the level in the short arm by an amount equal to the barometric pressure (unless we are near sea level this will be somewhat less than 760 mm). The gas is now confined at 2 atmospheres (atm) pressure, and its volume is found by actual observation to be 8 ml (Experiment 2). *It is understood that we are keeping the temperature of the gas constant, in this case at room temperature.* Similarly, at other pressures the gas will be found to occupy the volumes given in the table.

Thus, we find, from such a notebook record of our experimental measurements, that each time the pressure is doubled, the volume is diminished by half. In other words, the product of the pressure and the volume is constant throughout the series of measurements. Stated in algebraic form, we have the equation

$$P_1V_1=P_2V_2=P_3V_3=K, \quad (1)$$

in which P_1 and V_1 are the pressure and volume of a given mass of gas under one set of conditions, P_2 and V_2 those under another. K is their constant product. The numerical value of K will, of course, depend upon the weight of gas taken for experimentation and the units of measurement employed.

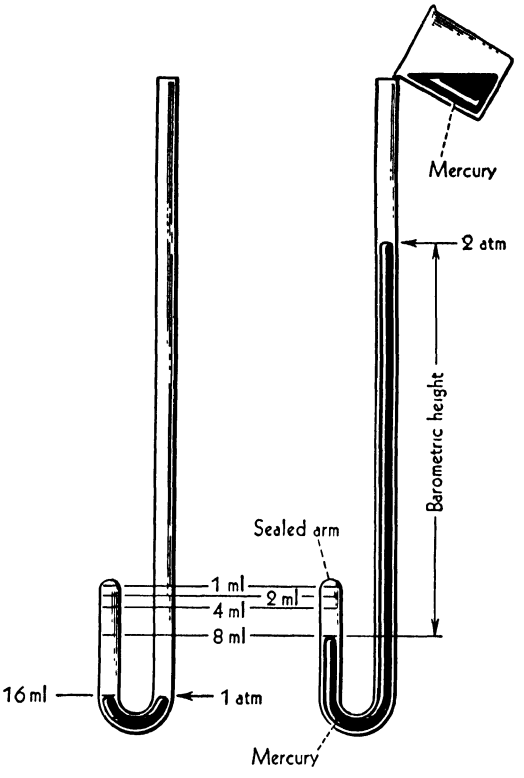


Fig. 6-5. Diagram of Apparatus Used for Showing How the Volume of a Gas Varies with the Pressure to Which It Is Subjected

Finally we may picture the results of our experiment graphically (Fig. 6-6). Representing the pressure along the *abscissa* (horizontal line) and the volume along the *ordinate* (vertical line), we plot the points found in Experiments 1, 2, 3, 4, 5, from our data and thus obtain the curve AB. The areas of the rectangles corresponding to P_1V_1, P_2V_2, P_3V_3, are all equal, and therefore *constant*. The curve is known in geometry as a rectangular hyperbola.

The generalization illustrated above is known as *Boyle's law* because it was first formulated in 1660 by Robert Boyle (Fig. 6-10), who made some careful measurements on the compressibility of air. Boyle's law may be stated thus: *The volume occupied by a given mass of a gas is inversely proportional to the pressure under which it is measured, at constant temperature.* To understand better the significance of the expression "inversely proportional," rearrange equation $P_1V_1 = P_2V_2$ to

$$\frac{V_1}{V_2}=\frac{P_2}{P_1}. \quad (2)$$

Now it is seen that the ratios of pressures and volumes have their subscripts arranged inversely. We may also write $PV = K$, or $V = K \times \frac{1}{P}$, which shows that the volume is inversely proportional to the pressure. (K is the proportionality constant.)

Example · Suppose that a gas, measured under a pressure indicated by a barometric reading of 720 mm, has a volume of 620 ml. What volume will this gas occupy under standard pressure (760 mm), with the temperature constant?

According to Boyle's law, $P_1V_1 = P_2V_2$. In this problem

$$P_1 = 720 \text{ mm}; \quad V_1 = 620 \text{ ml}; \quad P_2 = 760 \text{ mm}; \quad V_2 \text{ is to be calculated.}$$

Substituting these values in the equation, we have

$$720 \times 620 = 760 \times V_2, \text{ or } V_2 = 587.4 \text{ ml.}$$

NOTE Because an increase in pressure results in a contraction in volume, it is easy to see that the answer above is *qualitatively* correct because 587.4 ml is less than 620 ml

2. **Variation of volume with temperature; the law of Charles.** Jacques Charles, in 1787, discovered that all gases expand when the tempera-

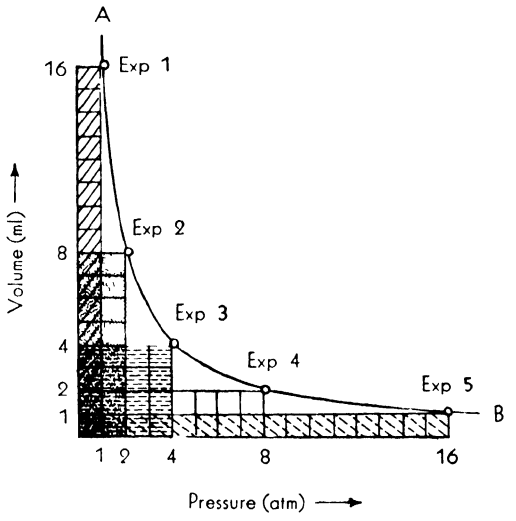


Fig. 6-6. Graphic Representation of the Experiment Illustrated in Fig. 6-5

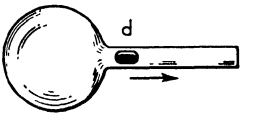


Fig. 6-7. Gas Confined in the Bulb at Constant Pressure by the Mercury Droplet, *d* Will Expand When Its Temperature Is Raised, and the Increase in the Volume Can Be Measured by the Displacement of the Droplet in the Side Tube

ture is raised (if the pressure is kept constant) and that equal volumes of all gases expand to the same extent for the same increase in temperature. This was confirmed in 1801 by Gay-Lussac (Fig. 6-11), using the apparatus shown in Fig. 6-7.

Let us take the simplest possible case and suppose that the volume of the gas has been measured at zero on the centigrade scale. Experiment shows that a rise of one degree causes an expansion equal to $\frac{1}{273}$ of this volume; a rise of two degrees, an expansion of $\frac{2}{273}$. That is to say, if 273 ml of the gas is measured at zero, the volume at 1° above will be 274 ml; at 2° above, 275 ml. At 1° below, it will contract to 272 ml, and at 2° below, to 271 ml (see Fig. 6-8). If the same rate of contraction should

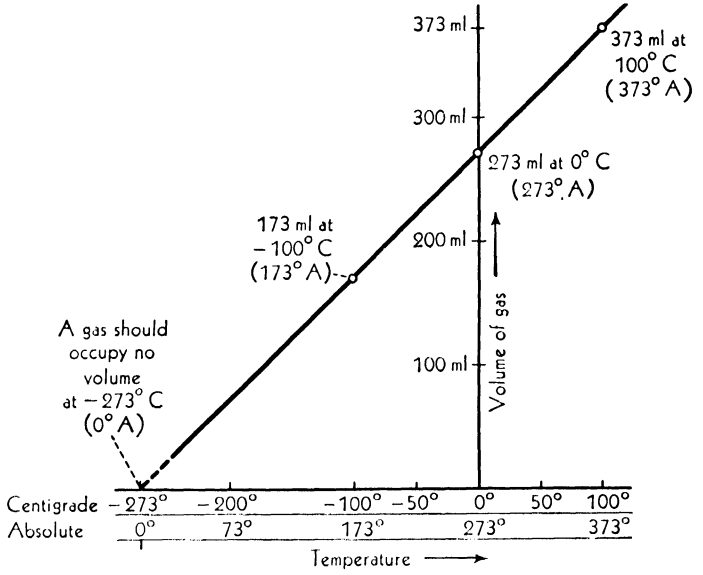


Fig. 6-8. Graphic Representation of the Variation of the Volume of a Gas with Temperature

hold good at all temperatures, then at $-272°$ the volume would be 1 ml, and at $-273°$ the volume would be zero. Obviously this conclusion cannot hold, since before such temperatures are reached all gases will have become liquids, in which state the law will not apply. For example, helium, the most difficult of all gases to liquefy, becomes a liquid at $-268.9°$.

The Absolute Scale · For many purposes it is desirable to use what is called the *absolute* or *Kelvin scale* of temperature rather than the centigrade scale. On this scale the degrees are the same size as on the centigrade scale, but the zero point is at $-273°$ centigrade, so that water freezes at 273° A (absolute) and at 0° C (centigrade). At 272° on this scale the 273 ml of gas discussed in the last paragraph would measure 272 ml; at 271°, 271 ml. On such a scale the volume of the gas is proportional to the temperature at every point. It will be noticed that the

absolute temperature is obtained by adding 273° to the centigrade temperature. Fig. 6-9 compares the centigrade and absolute scales.

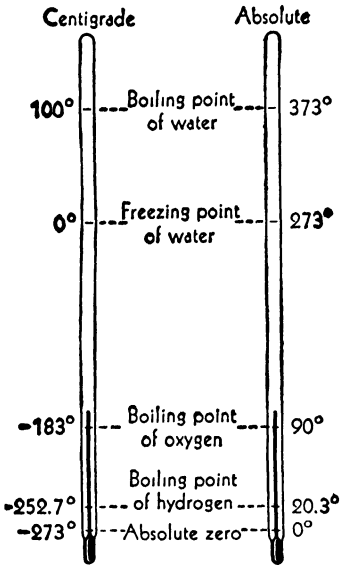


Fig. 6-9. Comparison of the Centigrade and Absolute Scales

The following general statement can now be made in regard to the variation of volume of a gas with temperature (Charles's law): *The volume occupied by a given mass of gas is directly proportional to the absolute temperature, at constant pressure.* If V_1 and V_2 are the volumes at the absolute temperatures T_1 and T_2, then

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}. \tag{3}$$

Example · The volume of a certain gas, when measured at a temperature of 70° C, is 650 ml. What is its volume at 10°?

First, reduce the centigrade readings to absolute:

70° C = (70 + 273) degrees absolute = 343° A
10° C = (10 + 273) degrees absolute = 283° A

According to Charles's law,

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}.$$

In this problem

$$T_1 = 343° \text{ A}; \quad V_1 = 650 \text{ ml}; \quad T_2 = 283° \text{ A}; \quad V_2 \text{ is to be calculated.}$$

Now, substituting these values in the equation, we have

$$\frac{650}{V_2} = \frac{343}{283}, \quad \text{or} \quad V_2 = \frac{650 \times 283}{343} = 536.3 \text{ ml}.$$

NOTE. Because a decrease in temperature results in a contraction in volume, we see that the answer above is *qualitatively* correct.

The Rankine Scale · An absolute temperature scale can also be set up in which the size of the degree is the same as on the Fahrenheit scale. Such a temperature scale is known as the Rankine scale and is widely used by engineers. Since 1° F corresponds to $\frac{5}{9}$° C, by simple arithmetic 0° Rankine (R) = − 460° F.

3. Variation of pressure with temperature: the law of Gay-Lussac. It was also shown experimentally by Gay-Lussac that *if the volume of a gas is kept constant, the pressure will increase in proportion to the absolute temperature:*

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}. \tag{4}$$

When an automobile tire "runs hot," or when gas cylinders become over-

heated, as in a laboratory fire, or when an explosion occurs in a space surrounded by thick, strong walls, the gas pressure increases with rising temperature, at substantially constant volume. With equation (4) the increased pressure may be calculated if the temperature is known, and vice versa.

Variations in Volume Due to Changes in Both Pressure and Temperature · In case both pressure and temperature change, then the calculation may be made for each in succession. It is more convenient, however, to combine equations (1) and (3), which express, respectively, Boyle's law and Charles's law, and use this new equation for the solution of such problems. This new equation is

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{5}$$

and may be derived as follows: Let us start with a given gas of initial pressure, volume, and temperature P_1, V_1, T_1, and take the gas, in two operations, to the final pressure, volume, and temperature P_2, V_2, T_2. First, we shall keep the temperature constant, and let P_1 change to P_2. Then $P_1V_1 = P_2V_x$, where V_x is some intermediate volume. Then, keeping the final pressure, P_2, constant, we shall allow T_1 to change to T_2. Therefore

$$\frac{V_x}{T_1} = \frac{V_2}{T_2}.$$

Solving this for V_x we get

$$V_x = \frac{V_2T_1}{T_2};$$

and substituting for V_x in the first equation, we have

$$P_1V_1 = P_2 \times \frac{V_2T_1}{T_2}, \quad \text{or} \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}.$$

This equation really embodies all three laws, those of Boyle, Charles, and Gay-Lussac.

Example · A gas measured 1000 ml at a temperature of 50° C and under a pressure of 740 mm. What volume will it occupy at a temperature of 27° and under a pressure of 760 mm?

By substituting the proper values in equation (5), namely, the values

$P_1 = 740$ mm; $T_1 = (273 + 50)°$ A; $V_2 = ?$;
$V_1 = 1000$ ml; $P_2 = 760$ mm; $T_2 = (273 + 27)°$ A,—

we have

$$\frac{740 \times 1000}{273 + 50} = \frac{760 \times V_2}{273 + 27}, \quad \text{or} \quad V_2 = 904.3 \text{ ml}.$$

To Check · Rewrite equation (5) to give $V_2 = V_1 \frac{P_1}{P_2} \frac{T_2}{T_1}$, which states that the final volume is equal to the original volume multiplied by two fractions, one to correct for a change in pressure and the other to correct for a change in temperature. Since the pressure change is from 740 mm to 760 mm, the volume is decreased and the fraction for pressure is $\frac{740}{760}$. Similarly the temperature change is from 323° A (50° C) to 300° A (27° C) (giving a decrease in volume), and the fraction for temperature is $\frac{300}{323}$. Thus $V_2 = 1000 \text{ ml} \times \frac{740}{760} \times \frac{300}{323}$, or 904.3 ml.



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Fig. 6-10. Robert Boyle (1627–1691) · Distinguished British scientist, founder of scientific chemistry. He was the first to define an element clearly and to show that a compound is made up of two or more constituents. He is chiefly remembered for his experimental work on gases, which led to his formulation of Boyle's law. He helped to perfect the air pump and proved that sound cannot pass through a vacuum. He is the author of an important book entitled *The Sceptical Chemist*, published in 1661.

Standard Conditions · In addition to the standard pressure, we must have a standard temperature. This is chosen as 0° C, or 273° A, at which temperature ice melts. These two conditions of temperature and pressure are known as the *standard conditions*. When the volume of a gas is given, say 100 liters of oxygen, it is understood that the gas occupies this volume under standard conditions (unless specified otherwise), namely, at a temperature of 0° C and under a pressure of 760 mm. The statement that 1 liter of oxygen weighs 1.4290 g means that 1 liter of this gas measured under standard conditions weighs 1.4290 g.



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Fig. 6-11. Joseph Louis Gay-Lussac (1778–1850) Distinguished French scientist. He showed the variation of the volume of a gas with its temperature, as did also Charles and Dalton about the same time; determined accurately the ratio by volume in which oxygen combines with hydrogen, as well as the combining ratio of many other pairs of gases, and so formulated the law of combining volumes (p. 132). He discovered cyanogen and made many improvements in analytical processes. He was one of the great teachers of his generation and held a number of public offices, including membership in the House of Peers.

It is not always convenient to measure gases at standard conditions; consequently it is often necessary to "correct," or "reduce," the volume of a gas collected at other than standard conditions to the volume that it would occupy at standard conditions.

Example of Correction to Standard Conditions · Suppose we have prepared oxygen in the laboratory and find that the gas measures 685 ml under the laboratory conditions, namely, a temperature of 22° and a barometric pressure of 750 mm, and we wish to know what volume this gas would occupy under standard conditions.

By substituting in equation (5) the proper values, namely the values

$P_1 = 750$ mm; $T_1 = (273 + 22)°$ A; $V_1 = 685$ ml;
$P_2 = 760$ mm; $T_2 = 273°$ A; $V_2 = ?$,—

we get

$$\frac{750 \times 685}{273 + 22} = \frac{760 \times V_2}{273}, \quad \text{or} \quad V_2 = 625.57 \text{ ml}.$$

This may be *checked* by the method outlined previously.

4. **Partial pressure of gases; the law of Dalton.** As a result of a large number of experiments which he conducted with *mixtures of gases*, Dalton (Fig. 3-5) concluded that *the total pressure exerted by a mixture of gases is the same as the sum of the individual pressures exerted by the constituent gases taken separately.* The essential meaning of this statement may be conveyed in another way: *In a mixture of gases every gas exerts the same pressure that it would if it alone were confined in the same volume, and the total pressure is simply the sum of these* ***partial*** *pressures.* In symbols we may state Dalton's law as follows:

$$P = p_1 + p_2 + p_3 + \cdots$$

For example, in the case of air the total pressure of any sample of air is the sum of the pressures of the oxygen gas, the nitrogen gas, the argon, the carbon dioxide, and the water vapor, which, taken together, make up the mixture known to us as air.

Collection of Gases over Liquids · Large tanks, floated on water, for the storage of fuel gas are to be seen in many cities; and chemists collect gases over liquids, in their laboratory manipulation. Gases will bubble up through a liquid into a reservoir space above; and the liquid may be used as a movable wall, or piston, for compressing a gas or allowing it to expand. Of all available liquids, chemists usually prefer to use mercury because it will not dissolve any gas, and because it is so slightly volatile that its vapor does not contaminate the gas collected above it, to any appreciable extent. At times, however, a chemist may not be in

possession of enough mercury to handle a large volume of gas; and mercury is attacked chemically by certain gases. He may then employ one of the oils. Water is frequently used; but water evaporates readily, and water vapor will saturate a gas in storage above the liquid water. If water is used, then some procedure must be devised for "correcting" for the presence of the water vapor, because a chemist is nearly always interested in calculating the volume of the dry gas at standard conditions.

Correction for the Presence of Water Vapor · Suppose a sample of oxygen has been collected over water in the graduated tube, *A* (Fig. 6-12), and it is required to find the volume which the *dry* oxygen would occupy under standard conditions. First, make the pressure inside the tube equal to the pressure outside by raising or lowering the tube until the levels of the water within and without the tube are the same, as shown in the figure. If the water levels inside and outside the tube were not the same, if, for example, the level inside were higher than that outside, we should know that the atmospheric pressure, pushing down on the outside surface, was greater than the gas pressure inside the tube and hence was forcing water up inside the tube. Conversely, if the level inside is below that outside, the gas pressure must be greater than the barometric pressure outside. When the levels are the same inside and out, the pressure must be the same inside and out, and we may determine the gas pressure in the tube by measuring the barometric pressure.

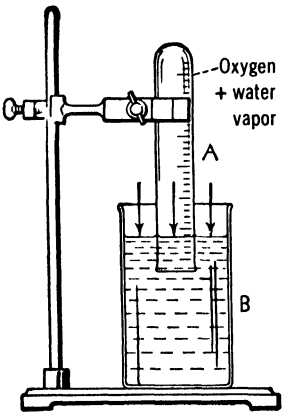


Fig. 6-12. Measuring the Volume of a Gas Collected over a Liquid

But part of the total pressure in the tube is due to the water vapor present. The magnitude of the vapor pressure of the water depends upon the temperature. The vapor pressures of water have been measured at various temperatures, and they are tabulated in the Appendix. To correct for the pressure of the water vapor, we measure the temperature of the water, find the appropriate value of the vapor pressure in the Appendix, and subtract this from the total pressure; and thus we obtain the pressure of the oxygen itself (Dalton's law of partial pressures).

Example · A gas, collected over water at 22°, had a volume of 1250 ml at a barometric pressure of 750 mm. Find the volume of the *dry* gas under standard conditions. The value of the pressure of water vapor at 22° is 19.8 mm (see Appendix).

$P_1 = (750.0 - 19.8)$ mm; $T_1 = (273 + 22)°$ A; $V_2 = ?$;
$V_1 = 1250$ ml; $P_2 = 760$ mm; $T_2 = 273°$ A.

Substituting in equation (5) we get

$$\frac{(750.0 - 19.8) \times 1250}{273 + 22} = \frac{760 \times V_2}{273}, \quad \text{or} \quad V_2 = 1119 \text{ ml.}$$

Deviations from the Gas Laws; Attractive Forces between Molecules. Although the gas laws which we have been discussing hold true fairly well for most gases under ordinary conditions, they do not hold true exactly. We should not expect them to do so except for an ideal gas—that is, for a gas whose molecules (for one thing) do not exert any attraction for one another. For example, it is a fact that when the pressure is increased to several atmospheres, the volume of most gases will decrease a little more than predicted by Boyle's law. The explanation is that the volume of a gas shrinks not only because the applied pressure squeezes the molecules more closely together, but also because the attractive forces of the molecules for one another tend to draw the molecules into a somewhat denser crowd. The applied pressure and the attractive forces work in the same direction.

These attractive forces, often called *van der Waals forces,* are physical in their nature and are not to be confused with forces of chemical attraction. They do not bring about chemical combination; but they do lead to the condensation of gases to liquids (and solids) and are responsible for holding the particles of a liquid together in a close-packed, coherent body. All atoms and molecules exert such attraction, but in varying degrees. The attraction exerted by water molecules is greater than that exerted by hydrogen molecules; hence water vapor is more easily condensed than hydrogen, and shows a greater deviation from Boyle's law than hydrogen.

5. **The rate of diffusion; the law of Graham.** In 1883 the Scotch chemist Thomas Graham made a series of studies upon what he called the rate of *diffusion* of gases, by which he meant the rate at which various gases will travel through another gas, through a minute pinhole, or through some porous materials such as unglazed pottery. As a result of his experiments he found that under definite conditions of temperature and pressure *the rate of diffusion is inversely proportional to the square root of the density of the gas,* or $v = \frac{k}{\sqrt{d}}$, where v represents the rate of diffusion and d the density, and k is a proportionality constant. Of two gases, No. 1 and No. 2, the lighter will diffuse more rapidly:

$$\frac{v_1}{v_2} = \frac{\frac{k}{\sqrt{d_1}}}{\frac{k}{\sqrt{d_2}}} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \sqrt{\frac{d_2}{d_1}}.$$

For example, oxygen and hydrogen have densities which are almost exactly in the ratio 16 : 1, and their rates of diffusion are approximately in the ratio

$$\frac{v_{\text{hydrogen}}}{v_{\text{oxygen}}} = \sqrt{\frac{d_{\text{oxygen}}}{d_{\text{hydrogen}}}} = \sqrt{\frac{16}{1}} = 4.$$

This means that molecules of hydrogen travel four times as fast, through a vacuum, or into another gas, or through a pinhole or a porous wall, as oxygen molecules.

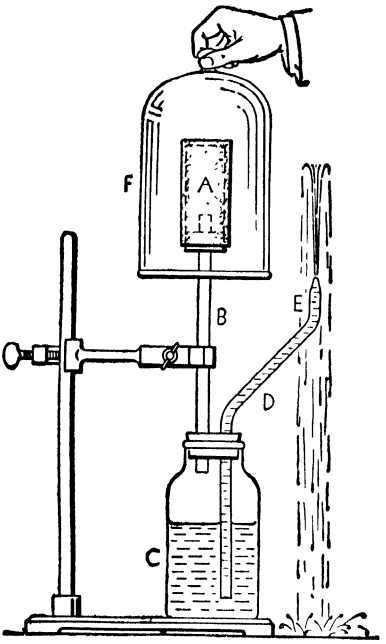


Fig. 6-13. Demonstration of Diffusion

Demonstration of Diffusion · When a bell jar or large beaker, *F*, is completely filled with hydrogen and quickly lowered over the *porous* jar, *A*, as shown, the hydrogen, being much less dense than the air, diffuses into the porous jar faster than the air within the jar diffuses out, and develops a pressure within the jar. This increased pressure is communicated to the surface of the water in the bottle, *C*, forcing some of the water out through the jet, *E*, and forming a fountain, as indicated

Essentially the same principle may be employed to effect the separation of the isotopes of uranium (Chap. 21). The hexafluoride of uranium, UF_6, is volatile enough to be handled as a gas. The density of the fluoride of U^{235} is slightly less than that of U^{238}. Consequently it diffuses a little more rapidly through a suitable porous wall; and if the portion of the gas mixture that passes through most easily is then allowed to diffuse repeatedly, a great many times, through such a porous wall, a considerable enrichment in the fluoride of U^{235} can be achieved.

The Kinetic-Molecular Theory

The Meaning of Laws in Science · The five laws just considered are merely general statements in regard to the conduct of gases *as determined by experiment*. Like all other scientific laws, they offer no explanation of the facts which they state, nor do they place any restriction upon nature which compels obedience, as the laws of a country bind society. They are simply concise statements of what might be called the *habits of nature* as observed in experiment.

Forming a Theory · Now that we have found it possible to describe in concise form (laws) the conduct of gases under varying conditions of

temperature and pressure, many questions arise in our minds. Why do all gases expand and contract in the same way, regardless of their other widely differing properties? Why does heating a gas cause it to expand? How does a gas exert pressure?

To answer these questions we begin by a process of *imagining*. We imagine that the similar conduct of all gases is probably due to some simple mechanical structure which they all share, and we try to form a mental picture of this structure. *The process of constructing a mental picture of this kind is called forming a theory.* After constructing a picture which answers all our questions, we then try to make the theory serve as the basis for the prediction of new effects, and try to find new facts and laws which will subject the theory to severe and critical test. Theories come and go: some, once highly respected, have been discarded because they could not stand the light of increased knowledge; a few have been recalled to life when later investigations demonstrated their validity. One of the most penetrating and far-reaching of all our theories, and one of the most fertile in prediction and forecast, is the famous *kinetic-molecular theory of gases.* So much evidence has now been collected in support of this theory that no one any longer doubts that it is a truthful picture of things as they really are.

The Kinetic-Molecular Theory of Gases · The theory that was developed about the middle of the last century to account for the properties of gases is known as the kinetic-molecular theory. The name implies that it is a theory about molecules in motion (*kinetic*). The essential postulates (assumptions) of this theory may be stated thus:

1. All gases are made up of extremely minute particles (molecules), separated at distances that are large compared with the size of the molecules themselves.
2. These molecules are in motion, and move in straight lines until they suffer a change of direction as a result of a collision with another molecule or with the walls of the containing vessel.
3. The collisions are perfectly elastic; that is, there is no average loss of energy as a result of them.
4. The kinetic energy of the moving molecules is proportional to the absolute temperature.

Molecular Motion · The ceaseless random motion, or thermal agitation, which molecules undergo is really *heat* itself, or rather the kinetic energy (motion energy) is heat. In terms of this heat-motion a great many effects of various sorts find their explanation. For instance, the tendency of a gas to spread, or *diffuse*, is to be attributed to the moving molecules,

darting here and there. The molecules travel at high velocity, like bullets, in straight lines except when they strike the walls of the containing vessel or bump into one another and bounce off like billiard balls. The pressure of a gas against the containing walls is the result of a continuous bombardment of the walls by the moving molecules, just as the flying fists of a fighter in the prize ring push his opponent back against the ropes. The magnitude of the pressure depends upon the rapidity of the bombardment - the number of collisions with the walls occurring in unit time - and the force with which the molecules strike. This concept of the pressure of a gas as the result of a bombardment of the walls by the moving molecules makes it possible to explain the observed pressure-volume-temperature relationships of gases as recorded in the gas laws.

Boyle's Law · Consider an idealized case in which there is only a single gas molecule in a container; let it be moving in a horizontal direction, so that it bounces back and forth from one wall to the other (*A*, Fig. 6-14). It will be moving at a certain speed, so that it will take a definite time to get back and forth. Suppose that the size of the container and the speed are such that it makes four thousand collisions with the right-hand wall in a certain time interval (say, one second), and in so doing produces a certain pressure. Now suppose that the volume of the vessel is decreased to one half by moving the wall on the right closer to the wall on the left (*B*, Fig. 6-14). In the same time interval as before, the molecule will make *eight* thousand round trips instead of four thousand, since it has only half as far to go. Hence it will make twice as many collisions with the right-hand wall as before, and the pressure, which depends upon the number of collisions in a given time, will be twice as great. This is Boyle's law, since halving the volume has doubled the pressure, or *the volume is inversely proportional to the pressure.*

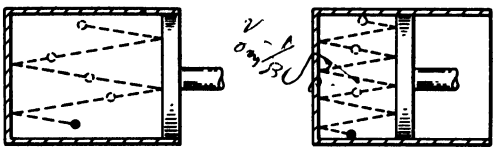


Fig. 6-14. Showing Motion of Gas Molecules in Container

Gay-Lussac's Law and Charles's Law · According to the fourth postulate of the kinetic-molecular theory, the kinetic energy is proportional to the absolute temperature. The kinetic energy of any moving particle is given by the expression $\frac{1}{2}mv^2$, where m is the mass and v the velocity. Since experiment shows that mass is not altered by a change in temperature, any change in the kinetic energy of a molecule that is produced by a change in temperature must come about by a change in the velocity with which the molecule is moving. Hence, if we return to the situation pictured in *A*, Fig. 6-14, and raise the temperature of the gas, the molecule

at the higher temperature will make the transit from wall to wall in a shorter time than before. Furthermore, since the molecule is moving faster, it will hit harder. As a result of these two effects (an increased frequency of impact and a greater impact), the pressure on the walls is increased at the higher temperature. This is Gay-Lussac's law, that *the pressure of a gas is proportional to the absolute temperature, at constant volume.* If the pressure is to be kept constant, then in order to compensate for the increased speed of the molecules, the walls must be drawn farther apart, so that they will not be hit as often. This is Charles's law, that *if the pressure is kept constant, the volume is proportional to the absolute temperature.*

Dalton's Law · Since, by the first postulate, a gas volume is made up largely of free space, it follows that in a mixture of gases the molecules of each type of gas are acting independently of the molecules of any other type. Hence *the partial pressure exerted by a single gas is that which it would exert if it alone occupied the total volume.*

Graham's Law · While the molecules of a given gas do not all have the same velocity (some travel faster than others), and so do not all have the same kinetic energy, there is an average velocity and an average kinetic energy. It is this average kinetic energy to which the fourth postulate of the kinetic-molecular theory refers. Maxwell was able to prove from the postulates of the theory that at any one temperature the average kinetic energy of the molecules of all gases is the same; specifically, for any two gases at the same temperature the average kinetic energy of the molecules of one gas is equal to the average kinetic energy of the molecules of the other. This is true, regardless of how large or small the masses of the two different molecules may be:

$$\tfrac{1}{2} m_1 v_1^2 = \tfrac{1}{2} m_2 v_2^2.$$

If m_1 is small, v_1 must be relatively large; if m_2 is large, v_2 is relatively small. Solving for v_1 and v_2, we obtain

$$\frac{v_1^2}{v_2^2} = \frac{m_2}{m_1}, \quad \text{or} \quad \frac{v_1}{v_2} = \frac{\sqrt{m_2}}{\sqrt{m_1}}.$$

The rate of diffusion is inversely proportional to the square root of the masses of the molecules, or the molecular weights. This is Graham's law, and this statement of it is equivalent to that given previously (p. 73): *The rate of diffusion is inversely proportional to the square root of the density of the gas.*

The Scientific Method · What we have been saying in the last few pages is a beautiful illustration of the application of the scientific method

(p. 6). Measurements of various sorts, during the past two or three hundred years, were made in connection with gases; thus, *facts* were gathered, and this knowledge was organized and formulated in *laws*. Then a theory, the kinetic-molecular theory, was invented to explain the laws, and to give a plausible reason for the various ways in which gases behave. The theory was successful from the beginning, and was fortunate in having such masters as Rumford, Joule, Clausius, Maxwell, Kelvin, Boltzmann, Jeans, and Langmuir to nurse it along and develop it. The theory suggested further pioneering experimental work, and was itself gradually improved and strengthened until now it gives us a convincing and deeply satisfying insight into the nature of material-particle behavior.

Further Evidence that Matter Is Made Up of Minute Particles · We have just been showing how satisfactorily the kinetic-molecular theory will account for, and even allow us to *predict*, the gas laws. Conversely, to the extent to which the explanations afforded by the kinetic-molecular theory are convincing, we bolster our belief in the actual existence of the invisible molecules and in the various acts which we assume that they perform. Of course there are many effects, other than gas behavior, which we try to explain in terms of particles. Dalton's laws of chemical combination, the law of definite composition, and especially the law of multiple proportions (p. 27) find a most convincing explanation in terms of the individual atoms. In fact, there is probably nothing in all of chemistry and physics that is not explained, at least in part, by the workings of little particles of one sort or another.

We shall now present four classic lines of evidence for the particle structure of matter, to enrich the student's background of working knowledge. The first two arguments, involving diffusion in solution and the Brownian motion, are of the inference type. The last two are strikingly objective and appeal directly to the sense of sight or of hearing.

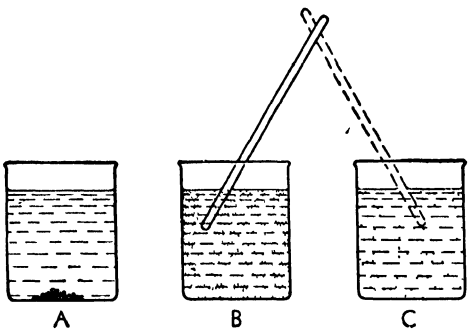


Fig. 6-15. Solution and Diffusion

1. **Solution and diffusion.** If we drop a few crystals of a colored dye into a beaker of water (*A*, Fig. 6-15), the crystals dissolve, and soon a deep color spreads throughout the entire volume of water (*B*). If we dip a glass tube into this and transfer a few drops of the colored solution to another beaker of fresh water (*C*), the color spreads again, although its in-

tensity is now much less. Our explanation of these effects is that the crystals of dye are made up of *particles* (molecules). These molecules themselves have color. The "dissolving" of the crystals is the breaking away of the molecules, which then move off into the water. The deep color of the solution in beaker *B* is to be attributed to the enormous number of molecules, billions of billions of them, spread out through the volume. If a relatively small portion of this large number of molecules is dipped up and dropped into the volume of water in beaker *C*, the resulting, more dilute solution will naturally possess less color than the more crowded system of molecules in beaker *B*. It is indeed difficult to conceive how any other explanation of the observed facts is possible.

2. **The Brownian motion.** Through a microscope of medium power it is easy to see fine dust floating in quiet air or, better still, the minute droplets of which tobacco smoke consists (Fig. 6-16). We notice that the droplets are dancing about, back and forth, up and down, in and out, with a restless haphazard sort of motion. This motion, named for an English botanist, Brown, who discovered it about one hundred and fifty years ago, can be explained satisfactorily only by assuming that the suspending medium (in this case, air) in which the droplets are floating is made up of molecules. These molecules are themselves possessed of random motion by virtue of their temperature energy, and they continually bump into the floating droplets and jostle them about. One cannot see the *molecules of air*, but one can see the direct effects of their impacts on the droplets.

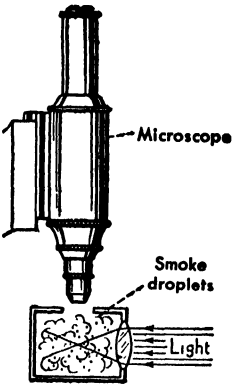


Fig. 6-16. Arrangement for Observing Brownian Motion

This observed Brownian motion is very convincing evidence for the existence of *particles* of matter; it is one of the classic arguments. Every student should avail himself of the opportunity of seeing this impressive spectacle.

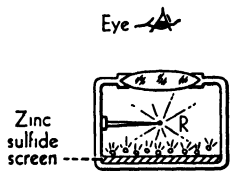


Fig. 6-17. Spinthariscope · The particles emitted from *R cannot* be seen — only the flashes of light where the particles strike the zinc sulfide screen

3. **The spinthariscope.** A zinc sulfide screen, over which are mounted a bit of radium, *R*, in Fig. 6-17 and a lens, is a device known as a *spinthariscope*. The name means an instrument for seeing scintillations, or glints of light. If the screen is observed in a dark room, it appears to glow, like a radium-treated watch dial. If one looks at the glow through the magnifying lens, one sees millions of tiny, individual flashes of light. Every flash is produced

by the impact on the screen of a *particle* (the so-called alpha particle) shot off during the disintegration of the radium. This alpha particle is an atom of helium having an electric charge. Seeing the separate flashes produced by the impact of individual atoms is almost as good as seeing the atoms themselves. Indeed, as we shall show a little later, a modified spinthariscope has *actually been used to count the helium atoms* that accumulate in this way, over a long time, to produce a small but measurable volume (or weight) of gas. It turns out that there are about 2.7×10^{16} atoms (or molecules) of helium in 1 mm^3 of helium, about 2.7×10^{19} in 1 ml, and about 6×10^{23} in 22.4 liters, or 4.003 g. (This 22.4 liters of gas volume, at standard conditions, is a common and convenient volume to deal with for reasons that will be explained later in our course.)

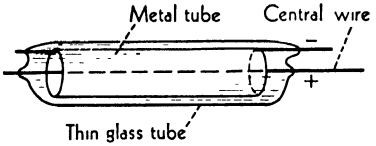


Fig. 6-18. Geiger Counter · A thin-wall, glass Geiger counter, with metal tube negatively charged and axial wire positively charged (about 1000 volts)

The Geiger Counter · A device which is sensitive to individual alpha particles and to electrons is the Geiger counter (Fig. 6-18). It is essentially an ionization chamber, and consists of a thin glass tube containing an ionizable gas or vapor, such as ethyl iodide, at low pressure, and two electrodes. One of these is a concentrically mounted metal tube, which is negatively charged; and the other is an axially placed wire, positively charged and connected to an amplifier. An alpha particle or an electron enters the ends of the chamber through its thin glass walls or thin mica window, collides with a gas molecule, and produces an electron and a positive ion. These, in turn, moving rapidly through the gas to the two electrodes (the wire and the metal tube) produce a whole set of electrons and ions, giving an eventual pulse in the amplifying circuit that is strong enough to actuate an indicating instrument such as a loud-speaker.

Thus single electrons and alpha particles may be counted. Since X rays and gamma rays cause ionization within the chamber, the intensity of even a feeble radiation coming, for example, from a uranium deposit may be evaluated.

Avogadro's Law · In 1811 the Italian Avogadro suggested what was known at that time as "Avogadro's hypothesis," namely, that *equal volumes of all kinds of gases at the same temperature and pressure contain the same number of molecules.* Avogadro proposed the idea originally to account for Gay-Lussac's law of combining gas volumes (a law which will be discussed in Chapter 9), and also because it seemed reasonable to Avogadro to believe that equal volumes of different gases, which contract

in the same way under applied pressure and expand *in the same way* with rising temperature, would themselves be constructed in the same way and would almost necessarily contain the same number of molecules.

Today Avogadro's hypothesis has been tested in so many different ways and verified so completely (within small limits of error) that we now call it *Avogadro's law.*

Avogadro's Law and Relative Weights of Molecules · Once we are sure that equal volumes of different gases under the same conditions contain *the same number of molecules,* we can compare the weights of different gas molecules. Let us weigh, on a chemical balance (p. 14), equal volumes (say, in liters) of the gases hydrogen, oxygen, and nitrogen, as accurately as we can. On page 13 we have already given the weight of 1 ml of hydrogen, 0.00008987 g, and the weight of 1 ml of oxygen, 0.001429 g. (Each of these weights was calculated from the weight of a liter of the gas.) Let us weigh also a liter of nitrogen. These weights, or liter-densities, at standard conditions of course, are as follows:

LITER-DENSITIES AND RELATIVE WEIGHTS OF THREE GASES

GAS	WEIGHT OF 1 LITER	RELATIVE WEIGHT
Hydrogen	0.08987 g	1
Oxygen	1.429 g	16
Nitrogen	1.251 g	14

Since there is the same number of molecules in every liter, the weights of these different molecules are related in the same way as the weights of the liters of gas, namely, Weight of molecule of hydrogen : weight of molecule of oxygen : weight of molecule of nitrogen = 0.0899 : 1.429 : 1.251, and the relative weights, on the basis of 1 for hydrogen, are approximately 1 : 16 : 14.

Such a means for measuring the relative weights of molecules will soon be developed (Chap. 9) as a method for the determination of *molecular weights.*

QUESTIONS

1. The statement "Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules" was first called a hypothesis; it is now called a law. (*a*) Why was this change made? (*b*) How is a theory related to a law and to a hypothesis?

2. Why did the early scientists learn more about the structure of gases than of solids and liquids?

3. Give instances that have come under your own observation showing the effect of (*a*) pressure and of (*b*) temperature upon the volume occupied by a given weight of gas.

4. State, in words and in equations, the laws or principles associated with the names of each of the following persons: (*a*) Boyle; (*b*) Gay-Lussac; (*c*) Charles; (*d*) Dalton; (*e*) Graham.

5. (*a*) Is it possible to change both the temperature of a given weight of gas and the pressure to which it is subjected, and yet have the volume remain constant? (*b*) Is it possible to change the temperature of a gas without changing either its volume or its pressure?

6. Suppose that a compressed gas were made to run an engine; what effect would this have on the temperature of the gas?

7. What becomes of the energy used in compressing a gas?

8. What additional statement is to be understood when we say that 1 liter of oxygen weighs 1.429 g?

9. Since the atoms of different elements, and therefore the molecules (made up of atoms) of compounds, have very different volumes, how can it be that 22.4 liters of *all* gases contain the same number of molecules?

10. In an experiment would it be possible to find that the volume of a gas, measured at a given temperature, had actually become smaller at a higher temperature?

11. What would be the effect of placing soft tennis balls in a vessel filled with hydrogen gas?

12. (*a*) In general, do Boyle's law and Charles's law hold true, regardless of the nature of a gas? (*b*) Why should they? (*c*) Should you expect any deviations from these laws to be greater at high pressures or at low pressures? (*d*) Why?

13. Enumerate the arguments which indicate that all matter is made up of particles.

14. Are there any features in the structure of atoms and molecules that would explain why there should be forces of attraction between them?

PROBLEMS

1. The volume of a gas at 1860 mm pressure is 10 liters. If the temperature is kept constant, what will the volume of the gas be at atmospheric pressure?

2. A certain quantity of gas occupies a volume of 700 ml at 720 mm pressure. Calculate what volume it will occupy at 840 mm pressure if the temperature is kept constant.

3. A gas occupies 880 liters at atmospheric pressure and 131°. If the gas is cooled at constant pressure to 30°, what will its volume be?

4. A quantity of nitrogen gas occupies a volume of 600 ml at a temperature of 27°. What volume will it occupy at − 3° if the pressure is unchanged?

5. A volume of 200 ml of hydrogen gas, measured at 21°, was heated under constant pressure until its volume was 300 ml. What was the final temperature, in degrees centigrade?

6. The pressure of hydrogen gas in a cylinder, at a temperature of 15°, is

60 atm, measured on a gauge. What would the gauge reading be if the temperature of the gas were raised to 39°?

7. What will be the volume, under standard conditions, of a gas which occupies 675 liters at 6 atm pressure and 117°?

8. A gas occupies 5 liters at 480 mm and − 73°. What will its volume be at 960 mm and 127°?

9. A certain quantity of gas was collected over water and was found to occupy 480 ml at 27° and 747 mm pressure. The gas was then dried and the volume measured at 57° and 660 mm pressure. What was the volume of the dry gas?

10. A quantity of oxygen, collected over water at 752 mm pressure and 23°, occupies 380 ml. What would the volume of this amount of pure oxygen be under standard conditions?

11. Calculate the pressure, in atmospheres, on the walls of a tank whose volume is 2 cu ft when 220 cu ft of air at atmospheric pressure is compressed into the tank, at constant temperature.

12. If the composition by volume of dry air is approximately 1 per cent argon, 21 per cent oxygen, and 78 per cent nitrogen, calculate by Dalton's law the partial pressure of each gas if the total pressure is 740 mm.

13. If 1 liter of hydrogen will leak out (by diffusion) through a small hole in 1 hour, calculate the time for 1 liter of the following gases to leak out under exactly similar conditions: oxygen, carbon dioxide, argon. (See the Appendix for the weight of 1 liter of different gases.)

14. (*a*) Calculate the volume of 10 g of hydrogen measured under standard conditions. (*b*) Suppose the pressure upon the gas were diminished from 760 mm to 700 mm, the temperature remaining constant; what volume would the hydrogen then occupy?

15. (*a*) Calculate the volume of 10 g of oxygen measured under standard conditions. (*b*) Suppose the temperature of the gas were increased from 0° to 18°, at constant pressure; what volume would the oxygen then occupy?

16. A certain quantity of gas occupies 24 cu ft at 14 lb/sq in. pressure and at 80° F. What would its volume be at 14 lb/sq in. and 20° F?

17. A certain quantity of gas occupies 2000 cu ft at 40° F and 1 atm pressure. Calculate the volume, in cubic feet, which this gas would occupy at 29.4 lb/sq in. and 90° F.

18. Calculate the number of molecules present in a quantity of gas which occupies 36,880 ml, at 745° and 380 mm pressure.

19. (*a*) Calculate the number of molecules in 2 liters of ordinary molecular oxygen measured at 25° and 770 mm pressure. (*b*) If the oxygen were converted completely to ozone, what volume would it occupy under standard conditions? (*c*) How many molecules of ozone would there be?

CHAPTER 7

HYDROGEN; HYDROGEN PEROXIDE

Hydrogen

Historical · The most abundant element in the universe is hydrogen; and of the total weight of matter in the universe hydrogen is estimated to be about 95 per cent. Most of the hydrogen that was probably present on the earth has escaped (p. 90); but some of it remains, combined with other elements in such compounds as water, ammonia, methane, the hydrocarbons of petroleum, and the immense variety of organic compounds out of which the tissues of plants and animals are made. The English investigator Cavendish (Fig. 7-1) is usually regarded as the discoverer of hydrogen because he was the first to get it in pure condition (1766) and to recognize it as an independent substance different from other known inflammable gases. Cavendish called the gas *inflammable* air, but later, when the gas was found to be a constituent of water, Lavoisier renamed it *hydrogen*, from two Greek words meaning "water former."



Fig. 7-1. Henry Cavendish (1731–1810) A famous English scientist, contemporary with Joseph Priestley. He described hydrogen as a new gas, and showed that it produced water when burned.

Occurrence · Free hydrogen is found in the lower atmosphere only in very minute amounts, and in the gases issuing from volcanoes. The spectroscope reveals huge quantities of the free element in the sun and certain other stars. Combined with oxygen in the form of *water*, it is widely distributed. Combined with carbon, it forms a large number of important compounds known as *hydrocarbons*, which constitute by far the greater part of *natural gas* and *petroleum*. It is likewise a constituent of the compounds present in living organisms and of most of the products derived from them, such as sugar, starch, fat, and protein.

Laboratory Preparation of Hydrogen · Since hydrogen is not found in the free condition to any appreciable extent, it must be prepared from

its compounds. The ones most often used as sources of hydrogen are (1) *water*, (2) *acids*, and (3) *bases*.

1. **Preparation from water.** Hydrogen may be liberated from water by two general methods: (*a*) by the action of the electric current, as described under the methods for the preparation of oxygen (p. 49); (*b*) by the action of certain metals. A few metals, such as sodium, potassium, and calcium, act rapidly upon water even at ordinary temperatures, liberating one half of the hydrogen present in the water acted on (Fig. 7-2). The remainder of the hydrogen, together with all the oxygen, combines with the metal to form compounds known as hydroxides. We may represent the reaction between sodium and water as follows:

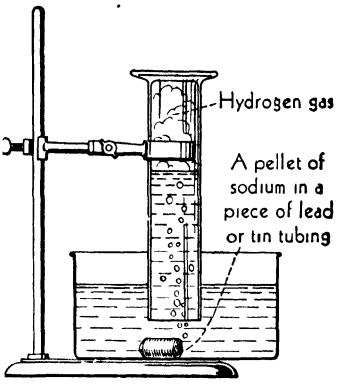


Fig. 7-2. Diagram Illustrating the Method of Preparing Hydrogen by the Action of Water on Sodium

$$\underset{\text{sodium}}{2\,Na} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{sodium hydroxide}}{2\,NaOH} + \underset{\text{hydrogen}}{H_2}\uparrow \qquad (1)$$

NOTE. A vertical arrow, pointing up, placed after the formula of an element or compound (see $H_2\uparrow$ above) indicates that the substance is a gas and, under ordinary conditions, will be given off in that form.

Other metals, such as magnesium and iron, also decompose water rapidly, but only at high temperatures. In such cases the decomposition is best effected by heating the metal to redness in a tube of iron or porcelain and then passing steam over the red-hot metal (Fig. 7-3). Under these conditions the metal and the oxygen of the water form an oxide, while the

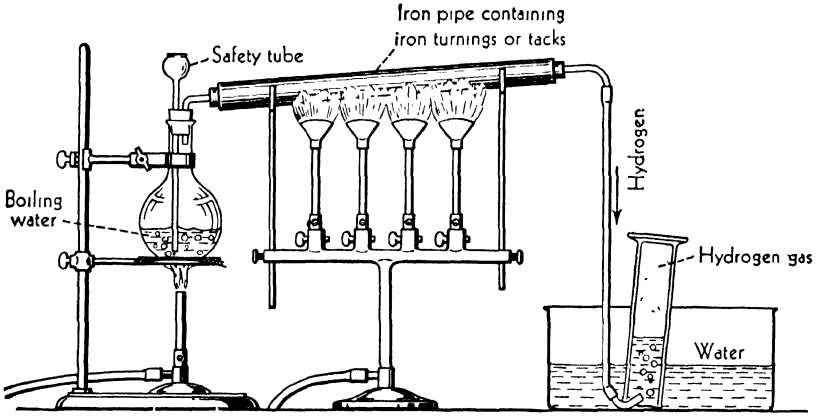


Fig 7-3. Diagram Illustrating the Method of Preparing Hydrogen by the Action of Steam on Iron

hydrogen is liberated. With iron, the equation for the reaction is

$$\underset{\text{iron}}{3\,Fe} + \underset{\text{water}}{4\,H_2O} \longrightarrow \underset{\text{iron oxide}}{Fe_3O_4} + \underset{\text{hydrogen}}{4\,H_2}\uparrow \qquad (2)$$

The oxide Fe_3O_4 is a compound of the oxides FeO and Fe_2O_3.

2. **Preparation from acids.** The *acids* are an important class of compounds containing hydrogen, which is liberated when the acid is brought into contact with certain metals. This reaction suggests a simple and convenient method for preparing hydrogen in the laboratory. Usually *zinc* or *iron* is used, with *hydrochloric acid* or *sulfuric acid.* Hydrochloric acid is an aqueous solution of a gaseous compound called *hydrogen chloride* (HCl), while sulfuric acid is an aqueous solution of an oily liquid known as *hydrogen sulfate* (H_2SO_4). To liberate hydrogen from these acids it is only necessary to bring the acid, properly diluted with water, into contact with the metal. The metal gradually passes into solution, while the hydrogen of the acid is in turn set free (Fig. 7-4). The liberation of the hydrogen is indicated by the bubbles rising in the liquid. When zinc and sulfuric acid are used in the preparation, the reaction may be represented as follows:

$$\underset{\text{zinc}}{Zn} + \underset{\text{sulfuric acid}}{H_2SO_4} \longrightarrow \underset{\text{zinc sulfate}}{ZnSO_4} + \underset{\text{hydrogen}}{H_2}\uparrow \qquad (3)$$

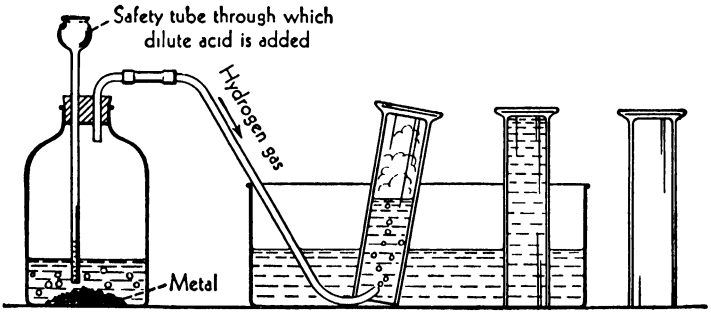


Fig. 7-4. Diagram of Apparatus Used for Preparing Hydrogen by the Action of an Acid on a Metal

It will be noted that the zinc simply takes the place of the hydrogen in the acid. The resulting compound of zinc, sulfur, and oxygen, known as zinc sulfate, is a colorless solid which remains dissolved in the excess water and may be obtained by evaporating the solution.

When iron and hydrochloric acid are used in the preparation of hydrogen, the reaction may be represented as follows:

$$\underset{\text{iron}}{Fe} + \underset{\text{hydrochloric acid}}{2\,HCl} \longrightarrow \underset{\text{iron chloride}}{FeCl_2} + \underset{\text{hydrogen}}{H_2}\uparrow \qquad (4)$$

Aluminum reacts with hydrochloric acid as follows:

$$\underset{\text{aluminum}}{2\,Al} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{6\,HCl} \longrightarrow \underset{\substack{\text{aluminum}\\\text{chloride}}}{2\,AlCl_3} + \underset{\text{hydrogen}}{3\,H_2}\uparrow \qquad (5)$$

The compounds formed (zinc sulfate, iron chloride, aluminum chloride) when metals react with acids in this way are known as *salts.*

Electrochemical Series · The question may be asked whether *all* metals will react with water or acids to produce hydrogen. The answer is No. If copper, for example, is added to sulfuric acid, no hydrogen is formed. By making a number of experiments of this sort, adding various metals to an acid, we may separate the metals into two groups:

DISPLACE HYDROGEN FROM ACIDS	DO NOT DISPLACE HYDROGEN FROM ACIDS
Zinc	Copper
Iron	Silver
Aluminum	Bismuth
Magnesium	

A reasonable extension of this information would be to find out whether these metals will displace one another from their compounds, and experiments can be made to find out whether zinc, for example, will displace iron, magnesium, or copper from the compounds of these metals in solution. It is found that these reactions take place:

$$\underset{\text{zinc}}{Zn} + \underset{\substack{\text{iron}\\\text{sulfate}}}{FeSO_4} \longrightarrow \underset{\substack{\text{zinc}\\\text{sulfate}}}{ZnSO_4} + \underset{\text{iron}}{Fe}$$

$$\underset{\text{zinc}}{Zn} + \underset{\substack{\text{copper}\\\text{sulfate}}}{CuSO_4} \longrightarrow \underset{\substack{\text{zinc}\\\text{sulfate}}}{ZnSO_4} + \underset{\text{copper}}{Cu}$$

but that no such displacement occurs when zinc is added to a solution of magnesium sulfate. On the other hand, magnesium added to zinc sulfate will produce magnesium sulfate and zinc:

$$\underset{\text{magnesium}}{Mg} + \underset{\substack{\text{zinc}\\\text{sulfate}}}{ZnSO_4} \longrightarrow \underset{\substack{\text{magnesium}\\\text{sulfate}}}{MgSO_4} + \underset{\text{zinc}}{Zn}$$

We then say that zinc is more reactive than iron and copper (and hydrogen), but magnesium is more reactive than zinc, and we have the beginnings of a *list of the metals in the order of their reactivity.* This list can be extended with other similar experiments until we have all the metals arranged in order. A few of them are so arranged in the accompanying list. Here the most reactive metal of those considered is at the top and the least reactive at the bottom. Any metal which is above another metal

in this list will displace the lower metal from its compounds. Thus, magnesium will displace iron or copper from iron or copper compounds:

$$\underset{\text{magnesium}}{Mg} + \underset{\substack{\text{iron}\\\text{chloride}}}{FeCl_2} \longrightarrow \underset{\substack{\text{magnesium}\\\text{chloride}}}{MgCl_2} + \underset{\text{iron}}{Fe}$$

$$\underset{\text{magnesium}}{Mg} + \underset{\substack{\text{copper}\\\text{chloride}}}{CuCl_2} \longrightarrow \underset{\substack{\text{magnesium}\\\text{chloride}}}{MgCl_2} + \underset{\text{copper}}{Cu}$$

Potassium
Calcium
Sodium
Magnesium
Aluminum
Zinc
Iron
Nickel
Hydrogen
Copper
Bismuth
Mercury
Silver

and it will displace hydrogen from acids. The reverse of these reactions will not take place; if copper is added to magnesium chloride, no reaction occurs. If copper is added to hydrochloric acid (HCl), no reaction occurs either, since copper is below hydrogen in the series, and hence cannot displace hydrogen from its compounds.

The list shown is a portion of the *electrochemical series*, so named because quantitative information telling how much more reactive one metal is than another may be obtained from electrochemical measurements (Chap. 13). We may now formulate the rule that *a metal above hydrogen in the electrochemical series will react with acids, and, under certain conditions, with water, to produce hydrogen.*

Equivalent Weight · It is convenient to record the weights of various metals which will produce a given weight of hydrogen by displacement of hydrogen from its compounds. For reasons given in Chapter 9, we choose 1.008 g of hydrogen as that given weight of hydrogen and define *the equivalent weight of a metal* as *that weight which will produce 1.008 g of hydrogen.* The equivalent weights of metals may be found by measuring the amounts of hydrogen produced in reactions represented by equations (1), (3), (4), and (5).

Example · It is found by experiment that 1.52 g of magnesium (Mg) will produce 0.126 g of hydrogen on reacting with hydrochloric acid. Hence the equivalent weight of magnesium is

$$\frac{1.52}{x} = \frac{0.126}{1.008}, \quad \text{or} \quad x = 12.16 \text{ g}.$$

Similarly the equivalent weights of sodium, zinc, and aluminum are found to be 22.997 g, 32.69 g, and 8.99 g respectively.

Commercial Methods for the Preparation of Hydrogen · A number of methods are employed in preparing hydrogen on a large scale for commercial uses.

1. The principal method, known sometimes as the *Bosch process*, consists in passing steam over highly heated carbon in the presence of a suitable catalyst. Carbon monoxide (CO) and hydrogen are first formed as shown in the following equation:

$$H_2O + C \longrightarrow CO + H_2$$

The resulting carbon monoxide then reacts with the steam, forming carbon dioxide (CO_2) and hydrogen:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The carbon dioxide is separated from the hydrogen by passing the mixture through water under pressure; the carbon dioxide dissolves in the water and leaves the hydrogen pure or nearly so.

2. A second important process consists in the action of steam on methane (CH_4), a hydrocarbon that constitutes the principal part of natural gas. The equations for the reactions involved are as follows:

$$CH_4 + H_2O \longrightarrow CO + 3\,H_2$$
$$CO + H_2O \longrightarrow CO_2 + H_2$$

The resulting carbon dioxide and hydrogen are separated as in the Bosch process. In a similar way, hydrogen may be obtained from other hydrocarbons (compounds made up of hydrogen and carbon).

Some hydrogen is also prepared by the electrolysis of water and by the action of steam on iron. Hydrogen is set free in the manufacture of certain important substances, such as chlorine (Chap. 15) and the alcohol known as butanol. This is known as *by-product hydrogen* and is utilized whenever possible. For many purposes, especially where complete freedom from air and moisture is desired, hydrogen may be obtained in a 3 : 1 mixture with nitrogen by the catalytic decomposition of ammonia. The use of hydrogen in this manner greatly reduces transportation costs because 100 lb of liquid ammonia may be shipped in a container weighing no more than the heavy cylinder required for 200 cu ft of hydrogen, and yet the 100 lb of ammonia may be decomposed to give about 3300 cu ft of hydrogen at the point where it is to be used.

Hydrogen is formed by the action of bases such as sodium hydroxide (NaOH) on silicon and on metals like zinc and aluminum:

$$Si + 2\,NaOH + H_2O \longrightarrow Na_2SiO_3 + 2\,H_2$$

Properties · Hydrogen, like oxygen, is a colorless, odorless, and tasteless gas. The solubility of hydrogen in water is very small, only about one half that of oxygen. Hydrogen is the lightest of all known substances,

14.385 times lighter than air; 1 liter of it weighs only 0.08987 g under standard conditions. It may be transferred from one vessel to another by being poured upward. Like the oxygen molecule, the hydrogen molecule contains two atoms, as shown in the equations above.

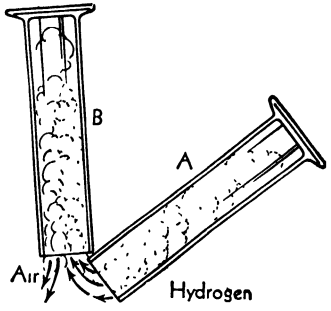


Fig. 7-5. The Hydrogen from Cylinder A Rises to the Top of Cylinder B and Displaces the Air

Velocity of Hydrogen and Other Molecules · We know that the velocity which gas molecules have is inversely proportional to the square root of their densities (Graham's law, p. 73). Light molecules move faster than heavy ones. The table below gives the average velocities of travel, in centimeters per second, at 0° C for the molecules of several of the gases present in the atmosphere.

A velocity of 1 mile/sec is about 16.1×10^4 cm/sec. Hence, of the gas molecules listed in the table below, hydrogen travels a little faster than 1 mile/sec, and carbon dioxide only about $\frac{1}{4}$ mile/sec. The projectile from the longest-range guns travels about 17×10^4 cm/sec.

DENSITIES AND AVERAGE MOLECULAR VELOCITIES OF SEVERAL GASES

GAS	DENSITY, GRAMS PER LITER	AVERAGE MOLECULAR VELOCITY AT 0° C
Hydrogen (H_2)	0.08987	18.39×10^4 cm/sec
Helium (He)	.1785	13.11×10^4 cm/sec
Nitrogen (N_2)	1 2506	4.93×10^4 cm/sec
Oxygen (O_2)	1.4290	4.61×10^4 cm/sec
Argon (A)	1 7824	4.13×10^4 cm/sec
Carbon dioxide (CO_2)	1.9768	3.92×10^4 cm/sec

Escape of Hydrogen from the Atmosphere · The question of why such a relatively small quantity of hydrogen is present in the earth's atmosphere is an interesting one, since it is likely that at one time the quantity was large, and it is likely that hydrogen is still being formed and liberated into the atmosphere. While the average velocity of hydrogen molecules is only a little greater than 1 mile/sec, some of the molecules acquire energy at the expense of other molecules with which they collide, and achieve velocities much in excess of the average. Such a fast-moving molecule, high in the atmosphere, could actually escape from the earth. Thus, gradually, over long periods of time, hydrogen has been dissipated from the atmosphere into outer space. The "escape velocity" is 1.1×10^6 cm/sec, or about 7 miles/sec, for any particle or body moving away from the earth.

The moon has no atmosphere at all, because the moon's gravitational attraction is so small that molecules even of the heavier gases may there attain the "escape velocity" of 2.4×10^5 cm/sec, or about 1.5 miles/sec.

Isotopes of Hydrogen · Experiments have shown that there are three kinds of hydrogen atoms, all alike in their chemical properties, but differing in their atomic weights as a result of different make-up of their nuclei. Such atoms are called isotopes.

1. *Light hydrogen, ordinary hydrogen,* by far the most abundant of the three hydrogen isotopes, has a single proton in its nucleus. Approximately 99.98 per cent of the hydrogen in the water on our planet is of this sort.

2. *Deuterium* has one proton and one neutron in its nucleus. It is present in water to the extent of 0.02 per cent, or 1 in 5000 parts. It

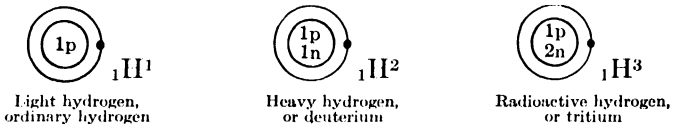


Fig. 7-6. Representing the Three Hydrogen Isotopes · The symbols, $_1H^1$, $_1H^2$, and $_1H^3$ indicate that each isotope has 1 proton, giving a single positive charge in the nucleus, but each has a different atomic weight, 1, 2, 3

may be concentrated by electrolysis of water, which liberates the light hydrogen as a gas at the cathode (negative pole) more readily than it does deuterium. The water is thus enriched with deuterium.

3. *Tritium* is often mentioned as a component of the hydrogen bomb. It was first discovered as a product in atomic reactors, and is now known to exist in nature, though in extraordinarily small amounts. It is formed in the atmosphere when fast neutrons, produced by cosmic rays, strike nitrogen atoms very hard, breaking them up into tritium and carbon atoms.

$$N + \text{neutron} \longrightarrow C + H^3$$

Tritium is radioactive. The total amount of tritium, most of it in the oceans, is only about two pounds! But thanks to its radioactivity and to extremely sensitive analytical techniques it is possible to measure accurately the amount of tritium in a single gallon of river water. We shall discuss radioactivity in later chapters.

Tritium atoms may be used as "tagged," or tracer, atoms, so that their progress through a complex series of reactions may be followed; and deuterium, though not radioactive, may also be traced by virtue of its density, which is twice as great as that of ordinary hydrogen.

The oxide of deuterium (D_2O) is known as *heavy water,* and has physical properties noticeably different from those of ordinary water, made from the natural mixture of hydrogen isotopes. It boils at 101.42°,

freezes at 3.82°, and has a specific gravity of 1.1059 at 20°. It is one of the substances used as a moderator in nuclear reactors (Chap. 21).

Liquefaction of Hydrogen · The English investigator Dewar was the first to obtain hydrogen in the liquid state. He cooled the gas to a very low temperature by means of liquid air, and at the same time subjected it to a pressure of 180 atm. In this way it was obtained as a colorless, transparent liquid, boiling at $-252.7°$ under a pressure of 1 atm. This is the lightest liquid known, having a density of but 0.07 at its boiling point. When liquid hydrogen is evaporated under very small pressure, solid hydrogen is obtained as a transparent, snowlike body melting at $-259.1°$.

Occlusion of Hydrogen · A large number of metals have the property of absorbing, or occluding, hydrogen. The quantity so absorbed by most of the metals is not large, but a few, especially platinum and palladium, take up large volumes of the gas. The quantity absorbed varies not only with the metal but also with the physical condition of the metal, as well as with the temperature and pressure under which the absorption takes place. One volume of palladium, in the form of a powder at ordinary temperatures, absorbs over 800 volumes of the gas. It is because of this property that hydrogen, when conducted into a hot tube made of iron or platinum, passes through the walls of the tube to a considerable extent.

The absorption of hydrogen by palladium can be strikingly shown by using strips of this metal as electrodes in the decomposition of water by the electric current. When the circuit is closed, oxygen is at once evolved at one electrode and hydrogen at the other. It will be noted, however, that the amount of hydrogen evolved as bubbles is relatively small at first, but gradually increases as the palladium becomes saturated with the gas.

Chemical Properties · Although hydrogen is inactive at ordinary temperatures, nevertheless under proper conditions it combines directly with many of the elements and even decomposes some compounds by uniting with elements present in them. Just as the compounds of oxygen with any other one element are called *oxides*, so those containing hydrogen in combination with another element are, as a class, known as *hydrides*, though this name is usually restricted to compounds of hydrogen with metals. Many of the nonmetallic hydrides have other names.

1. **Action of hydrogen upon elements.** At suitable temperatures hydrogen combines directly with sodium to form the solid sodium hydride (NaH); with nitrogen to form the gaseous compound known as *ammonia* (NH_3); with sulfur to form the gas known as *hydrogen sulfide* (H_2S); and

with chlorine to form *hydrogen chloride* (HCl). Although a mixture of hydrogen and chlorine does not react in the dark at room temperature, it explodes with great violence when exposed to direct sunlight.

Hydrogen is especially characterized by its affinity for oxygen, with which it combines to form water. Experiments show that the ratio in which these two gases combine is 1.008 parts of hydrogen to 8.00 parts of oxygen *by weight*, or 2 parts of hydrogen to 1 part of oxygen *by volume*. A large amount of heat is set free in this reaction. If we start with hydrogen and oxygen, at 25° and under a pressure of 1 atm, then for each gram of hydrogen entering into combination with the oxygen there is liberated 28,670 cal if the water produced remains in a state of vapor, or 33,880 cal if the resulting vapor is condensed to liquid form.

The union of hydrogen and oxygen, and the resulting formation of water, are shown by burning hydrogen in oxygen or air.

The hydrogen is generated in the flask, *A* (Fig. 7-7), and passed through the tube, *B*, filled with porous calcium chloride, which removes the moisture from the gas. *After the air has been displaced from the apparatus*, the hydrogen escaping at the jet is ignited. Almost instantly a dewlike substance is deposited on the cold sides of the jar, *C*. This may be collected, and, when its properties are examined, it proves to be water.

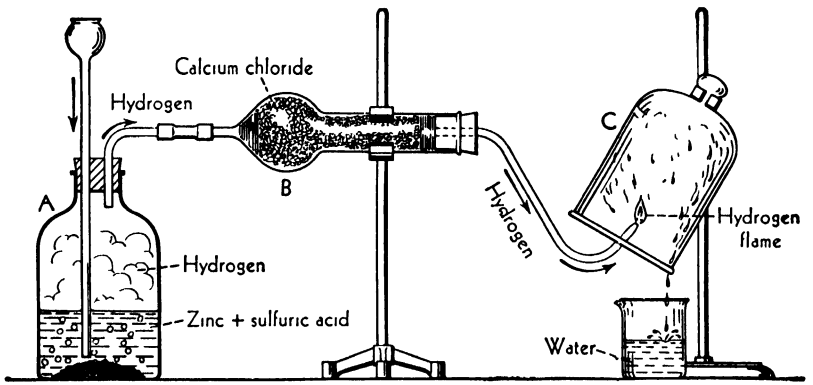


Fig. 7-7. Diagram of Apparatus Used for Burning Hydrogen in Air

The hydrogen, if pure, burns with a colorless but very hot flame. When the hydrogen is burned in air, much of the heat resulting from the union of the hydrogen and oxygen is absorbed in heating the inert nitrogen present. To obtain the maximum temperature one must use pure oxygen instead of air. Moreover, the hydrogen and oxygen must be brought together in the proportion in which they unite; otherwise the gas which is left uncombined will absorb a portion of the heat by being uselessly heated.

Explosion of a Mixture of Hydrogen and Oxygen · If hydrogen is to be burned safely in air (or in pure oxygen), it is necessary to make a proper arrangement of a flame burner for the hydrogen; otherwise mixtures of the gases within the explosive range, between 9 and 65 per cent by volume of hydrogen in air, will explode with terrific violence when ignited. This situation presents a constant hazard when working with hydrogen.

2. Action of hydrogen upon compounds. Hydrogen not only combines directly with many elements, such as chlorine and oxygen, when present in the free state, but under favorable conditions it will remove these elements from some of their compounds.

Action of Hydrogen on Copper Oxide · When hydrogen is passed through a tube containing hot copper oxide it combines with the oxygen to form water, which condenses in the colder portions of the tube, while the black color of the oxide of copper gradually gives way to the reddish tint of copper as the action progresses. The change may be represented as follows:

$$\underset{\text{hydrogen}}{H_2} + \underset{\text{copper oxide}}{CuO} \longrightarrow \underset{\text{water}}{H_2O} + \underset{\text{copper}}{Cu}$$

Many other metallic oxides, such as that of iron, may be substituted for the oxide of copper in this experiment. When oxide of iron is used, the change may be represented as follows:

$$\underset{\text{hydrogen}}{4\ H_2} + \underset{\text{iron oxide}}{Fe_3O_4} \longrightarrow \underset{\text{water}}{4\ H_2O} + \underset{\text{iron}}{3\ Fe}$$

Reduction; Reducing Agent · A compound from which oxygen is removed is said to be *reduced*, while the substance which removes the oxygen is called the *reducing agent*. Thus, in the reaction with the oxide of copper, the hydrogen is called the reducing agent and the copper oxide is said to be reduced. The process by which oxygen is removed from a

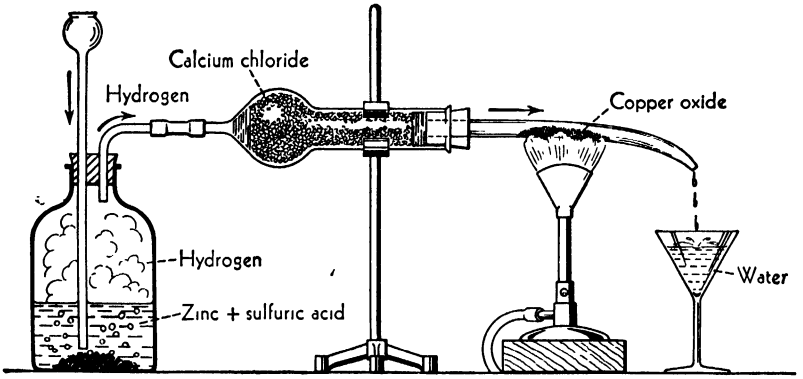


Fig. 7-8. Diagram of Apparatus Used for Reducing Copper Oxide with Hydrogen

compound is called *reduction*. It will be observed that reduction is just the reverse of oxidation. In the latter process oxygen is added to a substance, and in the former it is taken away. More comprehensive definitions of the terms *oxidation* and *reduction* will be given in a later chapter.

The Reaction between Hydrogen and Oxide of Iron · It will be observed that the reaction which takes place when hydrogen is passed over heated iron oxide (see above) is just the reverse of that which takes place when steam is passed over red-hot iron (equation (2), p. 86). In the one case hydrogen and iron oxide react to form water and iron; in the other the iron and water react to form iron oxide and hydrogen. Whether the reaction goes in the one direction or the other depends upon the conditions under which the reaction is carried out. If steam is passed over the iron, so that the hydrogen is swept away as fast as it is formed, there is none of the latter available to react on the iron oxide formed.

$$\underset{\text{iron}}{3\,Fe} + \underset{\text{water}}{4\,H_2O} \longrightarrow \underset{\text{iron oxide}}{Fe_3O_4} + \underset{\text{hydrogen}}{4\,H_2} \qquad (1)$$

On the other hand, if hydrogen is passed over the iron oxide, the reaction goes in the opposite direction, since the water is swept away as fast as it is formed.

$$3\,Fe + 4\,H_2O \longleftarrow Fe_3O_4 + 4\,H_2 \qquad (2)$$

If the reaction takes place in a closed vessel, so that the reaction products are not removed, both reactions go on at the same time, reaching a state of equilibrium.

$$3\,Fe + 4\,H_2O \rightleftarrows Fe_3O_4 + 4\,H_2 \qquad (3)$$

This matter will be discussed in detail in Chapter 24.

Physiological Action of Hydrogen · Pure hydrogen is not poisonous and may be breathed without danger, but the sulfuric acid and zinc used in its preparation frequently contain small amounts of arsenic, and the hydrogen generated from such substances is mixed with a gaseous compound of arsenic and hydrogen which is exceedingly poisonous and *must not* be inhaled.

Uses of Hydrogen · Enormous quantities of hydrogen are required to meet its many commercial uses. Chief among these are the following: (1) in the manufacture of ammonia, which is used in many ways, especially for the production of fertilizers: (2) for the "hardening" of certain vegetable and animal oils, such as cottonseed oil, whereby these oils are converted into solid or semisolid fats suitable for use as food and in the manufacture of soap; (3) for the "hydrogenation" of coal, whereby the coal is partially converted into lubricating oils, gasoline, and other prod-

ucts; (4) in the manufacture of methyl alcohol (known also as methanol and wood alcohol); (5) to provide a reducing atmosphere for furnaces for annealing and deoxidizing brass; (6) for preventing the oxidation in an electric furnace of tungsten and molybdenum wire; (7) for cooling large electric generators and transformers; (8) for many laboratory purposes.

Hydrogen was formerly used (and is still, to a limited extent) for inflating balloons and airships. The fact that it is combustible makes it a dangerous gas to use for this purpose, so that in America it is being replaced by the noncombustible gas helium.

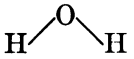
Hydrogen Peroxide

General · In addition to its common oxide, water, hydrogen forms another compound with oxygen known as hydrogen peroxide, discovered in 1818 by the French chemist Thénard. The proportions in which hydrogen and oxygen are present in the two compounds are

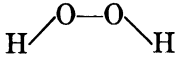
Water	1.008 parts of hydrogen to 8.000 parts of oxygen by weight
Hydrogen peroxide .	1.008 parts of hydrogen to 16.000 parts of oxygen by weight

In other words, *the weight of oxygen combined with a fixed weight of hydrogen is just twice as great in hydrogen peroxide as in water.* This corresponds to the difference between the formulas of the two compounds: H_2O for water, and H_2O_2 for hydrogen peroxide. The larger quantity of oxygen in the latter is indicated by the name *peroxide*; the prefix *per* means "more" or "excess."

We have already shown (pp. 41-42) that the electron formula or configuration for a water molecule may be written $H:\ddot{O}:H$ and that the bonds joining the H atoms to the O atom are not in a straight line. The angle between them is about 100°, thus:



The electron configuration for hydrogen peroxide is $H:\ddot{O}:\ddot{O}:H$ and the bonds here, too, make angles of about 100°:



Preparation · Dilute solutions of the compound are prepared by the action of acids on peroxides of the metals, the process being conducted at a low temperature so as to prevent the decomposition of the hydrogen

peroxide. For laboratory purposes one can readily obtain it in a solution, which also contains sodium chloride, by the action of hydrochloric acid on sodium peroxide:

$$\underset{\text{hydrochloric acid}}{2\,HCl} + \underset{\text{sodium peroxide}}{Na_2O_2} \longrightarrow \underset{\text{hydrogen peroxide}}{H_2O_2} + \underset{\text{sodium chloride}}{2\,NaCl}$$

Solutions are prepared commercially (1) by electrolysis of dilute solutions of sulfuric acid or ammonium sulfate or (2) by the action of acids on barium peroxide that has been hydrated with steam:

$$\underset{\text{sulfuric acid}}{H_2SO_4} + \underset{\text{barium peroxide}}{BaO_2} \longrightarrow \underset{\text{hydrogen peroxide}}{H_2O_2} + \underset{\text{barium sulfate}}{BaSO_4\downarrow}$$

NOTE. When a reaction in a solution leads to the formation of an insoluble substance, which therefore settles out, or *precipitates*, the sign ↓ is placed by the side of the formula of the precipitate (see the equation above).

The pure compound cannot be prepared without great difficulty, since it decomposes readily into water and oxygen, thus:

$$\underset{\text{hydrogen peroxide}}{2\,H_2O_2} \longrightarrow \underset{\text{water}}{2\,H_2O} + \underset{\text{oxygen}}{O_2\uparrow}$$

Properties · Hydrogen peroxide is a sirupy liquid, colorless unless seen through thick layers of the liquid, when it has a slightly bluish tint. Its density is 1.442 and its boiling point 152.1°. It freezes at − 1.7°. Its decomposition into water and oxygen is attended by the evolution of heat amounting to 676 cal for each gram decomposed.

Since hydrogen peroxide so readily decomposes, with evolution of oxygen, it acts as a strong oxidizing agent even in very dilute solutions. An easily oxidizable substance, like wool, is ignited by the addition of a few drops of the pure compound. The speed of decomposition of hydrogen peroxide is modified by many conditions. In dilute solutions and at a low temperature the speed is very slow, while at higher temperatures and in more concentrated solutions it becomes so great as to cause violent explosions. Moreover, it is greatly affected by the presense of certain catalysts (p. 48). Thus, a little manganese dioxide or finely divided platinum, added to a solution of the peroxide, greatly accelerates the evolution of oxygen gas. Certain organic substances, including those present in blood, have a similar action. Other substances have the opposite effect and retard the decomposition. Catalysts that retard the speed of a reaction are known as *negative* catalysts to distinguish them from *positive* catalysts, which increase the speed of a reaction. The commercial solution of hydrogen peroxide contains a small amount of a negative

catalyst to preserve its strength—usually a trace of acid or some organic compound (often acetanilide).

Uses · Hydrogen peroxide has many commercial uses, all based on its strong oxidizing properties. The common medicinal peroxide of the druggist is an aqueous solution containing 3 per cent by weight of the compound. This solution has been largely used as a germicide, but experiments indicate that it is not very effective for this purpose. Like ozone, it acts upon certain dyes and natural colors, such as that of the hair, oxidizing them into colorless compounds; consequently it is sometimes used as a bleaching agent. The chemist finds it especially useful as an oxidizing agent in many analytical operations. A 30 per cent solution, known as *perhydrol*, is now commercially available for chemical uses. Nearly 100 per cent solutions are used as the source of oxygen in some types of rockets.

QUESTIONS

1. Give definitions of (*a*) *reduction;* (*b*) *reducing agent;* (*c*) *oxidizing agent;* (*d*) *equivalent weight;* (*e*) *isotopes;* (*f*) *hydride;* (*g*) *negative catalyst.*

2. Contrast the properties of oxygen and hydrogen with respect to the following: (*a*) physical state; (*b*) color; (*c*) odor; (*d*) taste: (*e*) density, (*f*) solubility in water; (*g*) rate of diffusion.

3. (*a*) What products are formed as a result of the reaction of metallic sodium with water? (*b*) Write the equation for the reaction. (*c*) Write the equation for the reaction between sodium peroxide and hydrochloric acid.

4. What action will take place when iron (heated if necessary) is brought in contact with each of the following: (*a*) hydrochloric acid; (*b*) dilute sulfuric acid; (*c*) steam; (*d*) oxygen; (*e*) hydrogen? Write the equations.

5. Which of the following reactions will occur?

a. Zinc + copper sulfate (in solution) ⟶
b. Copper + sodium chloride (in solution) ⟶
c. Nickel + dilute sulfuric acid ⟶
d. Mercury + silver nitrate (in solution) ⟶
e. Calcium + water ⟶

6. Discuss the following statements. If a statement is true, explain why. (*a*) Reduction is the reverse of oxidation. (*b*) A hydrogen ion is a proton. (*c*) The molecule H_2 can be formed, from hydrogen atoms, but the molecule H_3 cannot be formed.

7. Why do you suppose that there is little or no hydrogen in the atmosphere?

8. Show why the statements "Sixteen per cent of the atoms in the combined atmosphere, hydrosphere, and earth's crust are hydrogen atoms" and "One per cent of the combined weight of the atmosphere, hydrosphere, and earth's crust is hydrogen" are not contradictory.

9. (*a*) What are deuterium and tritium? (*b*) What are the particles present in the nuclei of the atoms of ordinary hydrogen, deuterium, and tritium? (*c*) Write the equation for the reaction of deuterium oxide with metallic sodium.

10. What, would you say, are the various factors that determine the choice of the methods for the preparation of hydrogen (*a*) for laboratory purposes; (*b*) for industrial use?

PROBLEMS

1. Calculate the volume of 1 kg (*a*) of oxygen; (*b*) of hydrogen.

2. From the ratio, by weight, in which oxygen and hydrogen combine to form water, calculate the percentage of each of these elements in water.

3. Fifty liters of hydrogen and 40 liters of oxygen were mixed together in a strong vessel and heated until combination took place. (*a*) What substances were then present in the vessel? (*b*) Calculate the weight of each substance.

4. Calculate the heat evolved by burning 200 liters of hydrogen (measured under standard conditions) to form water vapor.

5. Suppose you wish to prepare 250 liters of hydrogen by the action of sulfuric acid on zinc. What weight of sulfuric acid containing 25 per cent of hydrogen sulfate would be required? HINT: hydrogen sulfate contains 2 per cent hydrogen.

6. One hundred milliliters of hydrogen gas was collected over water at 25° and at a barometric pressure of 740 mm. Calculate (*a*) the volume that this gas will occupy under standard conditions; (*b*) the number of hydrogen molecules present.

CHAPTER 8

THE ATMOSPHERE; NITROGEN, CARBON DIOXIDE, WATER, AND THE RARE GASES

The Earth and Its Atmosphere · The one feature which, as far as we know, distinguishes the earth from the rest of the universe is life itself and the peculiar fitness of the earth and its atmosphere to support life. Many scientists have been interested in this problem of the fitness of the environment.

Our earth is at such a distance from the sun that the average temperature (10° C) lies within the fairly narrow range in which protoplasm, as we know it, can exist. The earth's particular size gives rise to a gravitational force that is able to prevent the gas molecules of our atmosphere from escaping, by the normal processes of kinetic diffusion, into empty space. We have already alluded (p. 56) to the fact that if oxygen gas were diluted in the atmosphere by a somewhat larger proportion of nitrogen, fire would not burn, and also life (as we know it) might not be possible. The very presence of nitrogen and of carbon dioxide in the air is "vital," as we say, to life processes. Water itself has very unusual properties, perhaps ideal properties, almost as though designed for the role that it plays in the functioning of living matter.

The remarkable combination of factors and conditions in the material environment on the surface of the earth suggests that it would be interesting, in this present chapter, to discuss water and the other constituents of the atmosphere together.

Atmosphere and Air · The term *atmosphere* is applied to the gaseous envelope surrounding the earth; the term *air* generally indicates a limited portion of this envelope, as the air in a room, although the two words are often used interchangeably. Despite the fact that air is invisible, we are often conscious of its presence—for instance, in our breathing. On windy days we feel it beating against our cheeks and blowing through our hair. Air, of course, like other matter, possesses inertia.

Height of Atmosphere · It must not be supposed that the atmosphere is a layer of even thickness and of uniform density from bottom to top. As we climb a mountain or rise in an airplane, we find that the density and pressure decrease with increasing height. Finally, at great heights, the atmosphere fades out gradually into nearly empty space. At succes-

sive heights a given column of the atmosphere supports a smaller and smaller amount of air lying above it. At about 3.4 miles (18,000 ft) the density and pressure are only one half what they are at sea level. At a height of 50 miles the atmosphere is extremely rare; but even at 100 miles it is still dense enough to bring fast-moving meteors to incandescence by friction with the air.

The Atmosphere as a Great Chemical Storehouse · We have seen already (Chap. 6) that the atmosphere is everywhere pressing down on the surface of the earth with a pressure equal to that exerted by a column of mercury 76 cm high, or with a weight of 1033 g/cm^2. This is equivalent to about 15 lb/sq in. (more nearly 14.7), or more than 29 million tons over every square mile of the earth's surface. There are about 5700 million million tons in the whole atmosphere.

This great sea of air serves as a reservoir from which living organisms draw much of their sustenance. From it plants draw carbon dioxide, water, nitrogen, and oxygen; from it animal organisms draw oxygen directly, and nitrogen and carbon dioxide indirectly through the use of plants as food. Probably 99 per cent of our fuels have been made through natural processes from carbon dioxide, and of course it is the oxygen of the air in which these fuels burn. The chemical manufacturer takes nitrogen to make ammonia (NH_3) and nitric acid (HNO_3), and oxygen to convert sulfur into sulfuric acid (H_2SO_4), and the metallurgist takes vast quantities of oxygen to produce the heat needed for the smelting of metal ores.

The Substances Present in Air · The writings of Leonardo da Vinci and some of the ancient Chinese contain references to an active and an inactive constituent of the atmosphere; but the chemical investigators of the latter half of the eighteenth century were the first to demonstrate clearly the composite character of the atmosphere. The task was not fully completed until the closing years of the nineteenth century. A few simple experiments will convince us that air is a mixture of several different substances.

Water vapor. The evaporation of water and the condensation of moisture on cold objects suggest the presence of water vapor in the atmosphere. The moisture content of a given volume of air may be determined by passing the air through a cold trap, in which the water condenses or may even freeze. Also, the air may be passed through a tube containing some material such as calcium chloride (Fig. 7-7, p. 93), which readily combines with and retains water vapor. The increase in weight of such a tube is a direct measure of the weight of water vapor present in the sample of air.

Carbon Dioxide · When carbon dioxide is bubbled through a clear solution of calcium hydroxide ($Ca(OH)_2$), a white precipitate of calcium carbonate is formed, and this reaction serves as a good test for the gas:

$$\underset{\text{carbon dioxide}}{CO_2} + \underset{\text{calcium hydroxide}}{Ca(OH)_2} \longrightarrow \underset{\text{calcium carbonate}}{CaCO_3\downarrow} + H_2O$$

In this way one can prove the presence of carbon dioxide in the air, as well as in one's breath.

The percentage of carbon dioxide present in any sample of *dry* air is easily determined by passing a definite volume of the air through a tube containing soda lime (a solid mixture of sodium hydroxide and calcium hydroxide). The tube and contents are weighed both before and after the air is passed through the tube. The soda lime removes from the air all the carbon dioxide present, so that the increase in the weight of the tube and contents equals the weight of carbon dioxide in the air passed through the tube.

Oxygen and nitrogen. If a substance whose product of combustion is a solid is burned in a confined volume of air, the volume will decrease by about one fifth. This experiment may be conducted in the following manner: A piece of phosphorus, held by a wire, is ignited and is immediately covered with a vessel (containing air) inverted over water. The phosphorus combines with the oxygen to form an oxide, P_4O_{10}, called phosphoric oxide. This is a white, powdery solid which floats about in the air, but soon settles and is dissolved by the water. The removal of the oxygen is indicated by the rising level of water (Fig. 8-1).

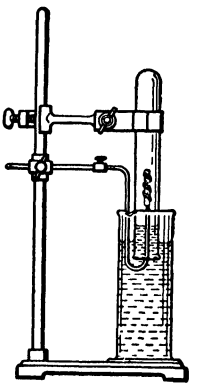


Fig. 8-1. Removing the Oxygen from Air by Using Phosphorus

The gas which remains (largely nitrogen) exhibits characteristics different from those of the original air: it does not support combustion, it is much less reactive than air, and it is incapable of supporting life.

Argon and other gases. The demonstration of the presence of the other constituents of the atmosphere is somewhat more difficult. It is necessary to free a sample of dry air, first, of its oxygen and carbon dioxide (as above), and then of its nitrogen. The latter operation is complicated not only by the large amount of nitrogen relative to the other remaining constituents but also by the sluggish reactivity of the nitrogen. On a small scale, the nitrogen may be removed by passing the gas sample over heated calcium, with which the solid, calcium nitride, is formed:

$$\underset{\text{calcium}}{3\,Ca} + \underset{\text{nitrogen}}{N_2} \longrightarrow \underset{\text{calcium nitride}}{Ca_3N_2}$$

The volume of gas remaining after such a series of operations, while definite in amount, is very small (less than 1 per cent of the total sample of air). This gas consists of argon mixed with minute percentages of the elements helium, neon, krypton, and xenon. These elements resemble nitrogen in many ways but differ from it in that they are completely inert toward chemical reagents.

The Separation of the Rare (Inert) Gases; Fractional Distillation · Because of the extreme chemical inertness of the rare gases, helium, neon, argon, krypton, and xenon, contained in this residue of air, physical methods must be used for their separation. It is possible to achieve some substantial separation by taking advantage of the different rates of diffusion (Chap. 6), that is, by allowing these gases to diffuse through a porous wall—for example, through porous clay. But a far more effective and more practical method is *fractional distillation*, which makes use of the difference in *boiling points* of the constituents of the mixture.

In order to have a very large quantity of starting material, liquid air itself (after water vapor and carbon dioxide have been removed) is distilled. It is placed in a suitable vessel and allowed to vaporize. The most volatile substances (those of lowest boiling point) evaporate first, and the least volatile last. The successive vapors in the volatility series are not entirely pure, as they have mixed with them, to some extent, the vapors of the more as well as of the less volatile substances; in other words, the separation is not clean-cut on first distillation. But the vapors may be collected separately, recondensed, and further purified by repeated distillations. The process just described is called *fractional distillation.*

Composition of Air · By the various methods, both chemical and physical, just described, it is possible to separate the mixture air into its

COMPOSITION OF DRY AIR

NAME	BOILING POINT IN DEGREES CENTIGRADE	BY VOLUME	BY WEIGHT
Nitrogen	− 195.8°	78.03 per cent	75.46 per cent
Oxygen	− 182.96°	20.99 per cent	23.20 per cent
Argon	− 185.8°	0.94 per cent	1.28 per cent
Carbon dioxide . .		3–4 in 10,000	0.045 per cent
Hydrogen	− 252.5°	1 in 1,000,000	
Neon	− 246.3°	1 in 65,000	1 lb in 44 tons
Helium	− 268.98°	1 in 200,000	1 lb in 725 tons
Krypton	− 152.9°	1 in 1,000,000	1 lb in 173 tons
Xenon	− 107.1°	1 in 11,000,000	1 lb in 1208 tons
Water vapor . . .	Variable within wide limits		

various constituents and to measure quantitatively their amounts in a sample of air.

The Constancy of the Composition of Air · Notwithstanding the changes constantly taking place which tend to alter the composition of air, the results of many analyses of *dry* air collected in the open fields show that the percentages of oxygen and nitrogen, as well as of carbon dioxide, are very nearly constant, not only from place to place, but from year to year. This constancy of composition in the case of oxygen is shown in the following analyses tabulated by Clarke. The percentages are expressed in volumes.

PERCENTAGE OF OXYGEN IN AIR			
LOCALITY OF SAMPLES	NUMBER OF ANALYSES	MINIMUM OXYGEN	MAXIMUM OXYGEN
Paris	100	20.913	20.999
Heidelberg	28	20.840	20.970
Manchester	32	20.780	21.020
Mountains of Scotland . .	34	20.800	21.180
Dresden	46	20.877	20.971
Cape Horn	20	20.72	20.970
Cleveland, Ohio	45	20.900	20.950

We do not know in detail why the composition of the air remains constant. Certainly the balance sheet embraces those processes by which gases are added to the atmosphere and those others by which they are taken away. Carbon dioxide is poured into the atmosphere, and oxygen withdrawn, by respiration, decay of organic matter, and combustion—forest fires and the burning of immense quantities of coal, wood, and oil. From these various sources as much carbon dioxide is furnished to the atmosphere every few years as is already present. On the other hand, the weathering of the rocks removes carbon dioxide in vast amounts, and growing plants not only remove carbon dioxide *from* but also give oxygen *to* the atmosphere. Perhaps all these opposing processes tend to offset each other. But it is very likely that the equilibrium exchange of gases between the atmosphere and the sea has a great deal to do with maintaining the constancy of the composition of the atmosphere.

Since we can obtain individual samples of all the substances present in air, we can examine them and study their properties and behavior. Oxygen, essential to life in all respiratory processes, has already been discussed in Chapter 5. We now consider nitrogen, carbon dioxide, water, and the inert gases.

Nitrogen

Occurrence · In the free condition nitrogen makes up about four fifths of the atmosphere, as we have already seen. In the combined state it is present in sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3), and in ammonia (NH_3) and its compounds. Nitrogen is likewise an essential constituent of proteins and many other "organic" compounds which are present in living organisms. The human body contains about 3 per cent of nitrogen.

Stability of the Nitrogen Molecule · Nitrogen gas is rather inert chemically. The two atoms of nitrogen in the molecule (N_2) are held together (covalent bonds) so strongly that a great deal of energy must be furnished to separate them. Since the two atoms must usually be separated before they may enter into combination with other elements, the free element is inactive at ordinary temperatures.

Preparation of Nitrogen from Air · For commercial purposes nitrogen is obtained entirely from liquid air by fractional distillation. In the laboratory it can be prepared by bringing air into contact with some substance that will combine with the oxygen but not with the nitrogen. The substances ordinarily used are phosphorus and copper, because they combine readily with the oxygen and because the oxides formed are *solids* and so admit of an easy separation from the remaining nitrogen. This slightly impure nitrogen, containing about 1 per cent of the rare gases, may be used for a study of most of the properties of the element, since these are not materially affected by the presence of the other gases. The method best adapted for preparing *pure* nitrogen in the laboratory consists in liberating the element from some of its compounds.

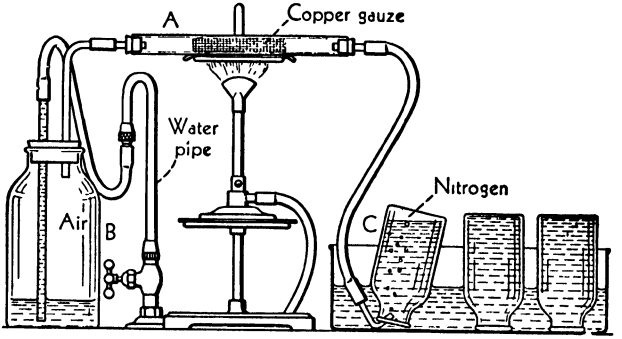


Fig. 8-2. Preparing Nitrogen by Passing Air over Hot Copper · The metal, in the form of gauze, is placed in a tube, *A*, and heated to a high temperature. The air is then forced slowly through the tube by allowing a small stream of water to flow into a bottle, *B*, connected with the tube, as shown in the figure. The oxygen combines with the hot copper and forms copper oxide (CuO), a solid which remains in the tube while the nitrogen passes on and is collected over water in the bottles *C*

Preparation of Nitrogen from Compounds · The compound that is most frequently used for the preparation of nitrogen is ammonium nitrite (NH_4NO_2). When heated, this compound decomposes into nitrogen and water, as represented in the following equation:

$$\underset{\text{ammonium nitrite}}{NH_4NO_2} \longrightarrow 2\ \underset{\text{water}}{H_2O} + \underset{\text{nitrogen}}{N_2}\uparrow \qquad (1)$$

Since ammonium nitrite is an unstable solid, it is convenient to substitute for it a mixture of sodium nitrite ($NaNO_2$) and ammonium chloride (NH_4Cl) In solution these two compounds react to form sodium chloride and ammonium nitrite:

$$NaNO_2 + NH_4Cl \longrightarrow NH_4NO_2 + NaCl \qquad (2)$$

As fast as it is formed, the ammonium nitrite decomposes into nitrogen and water, in accordance with equation (1).

The term *ammonium*, used in the names of such compounds as ammonium chloride, is applied to the covalent group of atoms NH_4, which is present in these compounds. It is an ion, positively charged, NH_4^+, called an *ammonium ion*. Both ammonium chloride and ammonium nitrite, as well as sodium chloride and sodium nitrite, are electrovalent compounds:

(NH_4^+, Cl^-), (NH_4^+, NO_2^-), (Na^+, Cl^-), and (Na^+, NO_2^-)

Properties of Nitrogen · Like hydrogen and oxygen, nitrogen is a colorless, odorless, tasteless gas. It is slightly lighter than oxygen; 1 liter of it weighs 1.2506 g. Like oxygen and hydrogen, it is only slightly soluble in water: 100 ml of water dissolves 2.33 ml of the gas under standard conditions. Liquid nitrogen boils at −195.8° and has a density of 0.8 at its boiling point. At low temperature and under high pressure, it is obtained in the form of an icelike solid (Fig. 8-3) which melts at −209.8°.

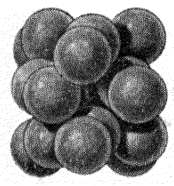


Fig. 8-3. Structure of Solid Nitrogen Crystal, Each Molecule Consisting of Two Atoms

Chemical Properties · Nitrogen is much less active than oxygen, showing little or no tendency to combine with any other elements at ordinary temperatures, because the N-to-N bond is the strongest bond formed by nitrogen. At high temperatures and under suitable conditions nitrogen combines with many of the elements. Thus, under the action of electric sparks or when it is heated in the presence of suitable catalysts, nitrogen combines with hydrogen to form *ammonia* (NH_3), and with oxygen to form *nitric oxide* (NO). Nitrogen likewise combines directly with silicon, boron, and titanium, and with a number of the metals, notably lithium, magnesium, and calcium. The compounds formed by the union of nitrogen

with another element are in general called *nitrides*, just as the compounds formed by the union of oxygen with another element are called *oxides*.

Industrial Uses of Nitrogen · The chief commercial use of free nitrogen is in the preparation of *ammonia* (NH_3) by direct combination with hydrogen; the ammonia, in turn, is used in the manufacture of fertilizers and other compounds of nitrogen, especially nitric acid (HNO_3), which is necessary for the production of explosives, photographic films, and lacquers. In smaller amounts nitrogen is used in the manufacture of other compounds, especially one called *cyanamide*. The process of manufacturing compounds of nitrogen from free nitrogen is known as the *fixation of nitrogen*. In view of the stability of the nitrogen molecule, the fixation of nitrogen is not an easy task, and much work was done in investigating possible methods before the modern process for ammonia synthesis was perfected.

Free nitrogen is used also for hardening steel and for filling the space in various vessels where an inert atmosphere is desired, such as the capillary space over the mercury in thermometers designed for use at temperatures ranging from 300° to 500°, the space in electric-light bulbs, and sometimes the space in the tubes, flasks, and bulbs that research chemists work with.

Importance of Nitrogen in the Metabolism of Plants and Animals · The element nitrogen is an essential constituent of all protein matter and of many other compounds present in living organisms. Yet, in spite of the fact that we are constantly immersed in a vast sea of free nitrogen, our bodies are not able to assimilate it directly, but must obtain their supply from the nitrogenous compounds present in such foods as milk, eggs, meat, beans, and peas. Plants do somewhat better; for some of them, in collaboration with certain strains of bacteria, parasitic on the roots of leguminous plants, are able to utilize the free nitrogen of the atmosphere and to convert it into compounds which we in turn can use. This constitutes a natural method for the fixation of atmospheric nitrogen. The amount of combined nitrogen present in the soil is, however, critical, and nitrogen compounds are therefore important constituents of fertilizers. Directly or indirectly, all the important compounds of nitrogen are formed from atmospheric nitrogen.

Carbon Dioxide

The Oxides of Carbon · The element carbon forms three oxides, carbon monoxide (CO), carbon suboxide (C_3O_2), and carbon dioxide (CO_2). Carbon dioxide is the most common, and is discussed at this time because it is present in the atmosphere. Carbon monoxide will be treated later.

Occurrence of Carbon Dioxide · Carbon dioxide gas is found in open air to the extent of about 3 parts in 10,000, a little higher in cities and a little lower in the country. This apparently small percentage is of fundamental importance in nature; for while the *percentage* of carbon dioxide in air is small, the *total amount* in the atmosphere is very large. In some localities it escapes from the earth in great quantities, and this is especially true of the oil-well and gas-well districts of Mexico and of some Western states. Many spring waters contain it in solution; when such waters reach the surface of the earth, the pressure upon them is diminished and the gas escapes as small bubbles (*effervescence*). Carbon dioxide is a product of the oxidation of all organic matter, and is therefore formed in all ordinary processes of combustion, as well as in those of decay. It is exhaled from the lungs of all animals in respiration, and is a product of many fermentation processes, such as that which takes place in the manufacture of alcoholic liquors.

Carbon Dioxide in Breath · According to Little, carbon dioxide "is normally present to the extent of about 4.5 per cent in human breath, and in a long life a man may exhale more than 20 tons of the gas. For the conduction of the process which results in its production, nature provides the average man with a lung area of about 100 sq yd," or enough for the floor space of a large room.

Quantity of Carbon Dioxide Formerly Present in the Atmosphere · On the basis of the known carbonate deposits, principally limestone beds, in the earth's crust, it has been estimated that at one time there was probably enough carbon dioxide present in the atmosphere to give a pressure of many atmospheres. At such high pressures the carbon dioxide, with the aid of water, attacked the bare granites and other igneous rocks, and combined with the lime (CaO) in these rocks to form calcium carbonate ($CaCO_3$). This was deposited directly as a sedimentary limestone or, after being carried in solution in river water to the sea, was there laid down in enormous beds made of the calcareous remains of shell-forming organisms. Thus, largely through the intervention of these carbonate-producing reactions, on a vast scale, by land and sea, over hundreds of millions of years, the atmosphere's content of carbon dioxide was diminished to what we know it to be at the present time. Even today, with much of the earth's rock surface covered over with a protective mantle of vegetation, and with the effective concentration of carbon dioxide only 3 parts in 10,000 of air, it has been estimated (by Chamberlain) that about 1,620,000,000 tons of carbon dioxide are withdrawn annually from the atmosphere by the chemical attack on the rocks.

Photosynthesis · But not all the carbon dioxide which disappeared from the atmosphere was removed by the weathering of the rocks. Plants

eventually began to grow, and they grew most luxuriantly under the hothouse conditions of those old times, millions of years ago. Plants utilize carbon dioxide. The green leaf of a plant may be regarded as a sort of chemical factory, where sunlight, in the presence of carbon dioxide, water, and the chlorophyll-containing cells of the plant, brings about a chemical reaction in which simple sugars are formed and oxygen evolved. The reaction is complex, but the outcome may be expressed by the following equation:

$$6\,CO_2 + 6\,H_2O \longrightarrow \underset{\text{a sugar}}{C_6H_{12}O_6} + 6\,O_2\uparrow$$

This process is called photosynthesis. While there are many steps in the process, between the first reaction of carbon dioxide and water and the formation of the sugars, and while some of these steps release energy and others require energy, the overall reaction is endothermic, absorbing heat; and the energy required to make the reaction proceed is supplied by the sunlight. The energy-traps which catch and remove the energy from the incident beam of sunlight are probably the chlorophyll molecules. Most of the energy which they receive is taken from the reddish-orange region of the spectrum (see the colored plate facing page 122). When reddish-orange light is absorbed from white light, the remaining light takes on the complementary color, green. That is why chlorophyll is green.

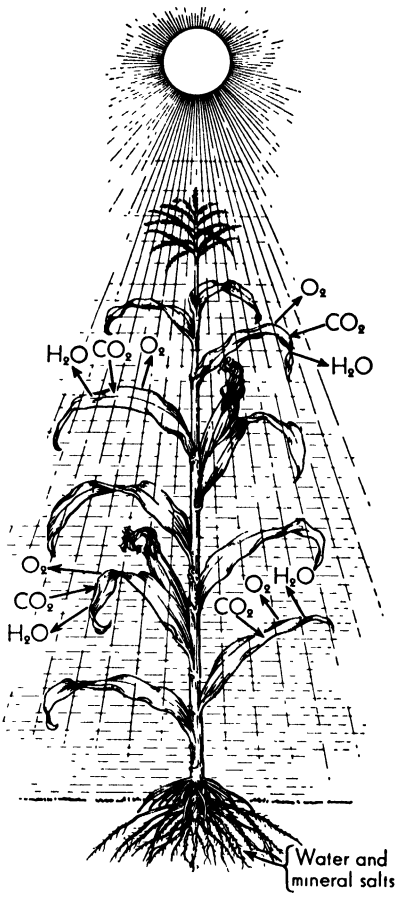


Fig. 8-4. Photosynthesis · The plant builds up (or synthesizes) carbohydrates, using water and mineral salts taken from the soil, and carbon dioxide from the air. Oxygen is set free in the process. The sunlight furnishes the energy that is required

The chlorophyll is contained in the chloroplasts (Fig. 8-5), which, in vast numbers, are located mostly in the palisade cells near the upper surface of the leaf, where the sunlight strikes. The area of the leaf surface of a tree may be very large; for instance, an elm tree of average size has about 7,000,000 leaves and about 5 acres of leaf surface. The carbon di-

oxide, from the air, enters the leaf through mouths, or stomata, on the underside of the leaf. Just how the chlorophyll molecules hand on to the molecules of carbon dioxide or carbonic acid the energy which they receive from sunlight is not yet known.

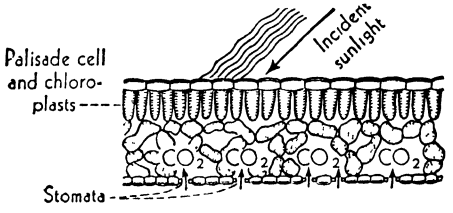


Fig. 8-5. Magnified Section of a Leaf

Importance of the Photosynthetic Process · The importance, in nature, of this chemical reaction may be judged from the following considerations:

1. **Foods.** Animals obtain their organic foods from plants, and plants in turn are dependent on the photosynthesis reaction. Sugars, starches, and cellulose are formed as products of photosynthesis; and the fats, proteins, vitamins, and other such foods are formed by further complex chemical reactions. Indeed, with few exceptions, it seems probable that *all the naturally occurring organic substances* originate directly or indirectly in photosynthesis.

2. **Fuels.** The sunlight energy used up in the decomposition of carbon dioxide in the leaf is stored as chemical energy in the oxygen and in the sugars, starches, and cellulose. All these organic substances are combustible; and if they are allowed to burn in air, carbon dioxide is reformed, the reactions are exothermic, and the original energy tapped off from the sunlight is yielded back as heat of combustion. It is in this sense that we may say that practically all our available energy comes from the sun. Wood (largely cellulose), by a slow process of change over a period of many millions of years, has been converted into peat, lignite, and finally coal; and probably oil and natural gas owe their origin to photosynthesis.

3. **Oxygen.** To photosynthesis we may also look for the possible explanation of how our atmosphere got its oxygen. There has been some speculation as to whether most of it might not have been set free from carbon dioxide by plants. The total weight of oxygen in the atmosphere is enormous, about $\frac{1}{5} \times 5.7 \times 10^{15}$ tons (p. 101). But if we consider that only about 3 lb of oxygen is present over every square inch of ground surface, it does not seem unreasonable that plant life could have brought about this final result, given hundreds of millions of years in which to accomplish it. Carbon, from which the oxygen of our atmosphere was separated, is now present in the earth's crust as graphite, coal, lignite, oil, hydrocarbon gases, and other carbonaceous materials.

Water

Introduction · Water is almost universal in its occurrence on our planet. It is present as ice and snow, as rain, as lakes and rivers, as a vapor in air, as underground waters, as an essential part of the soil, and as a constituent of many minerals. Vast areas of the colder regions of the globe are covered with ice. If the waters of the oceans, covering nearly five sevenths of the earth's surface, were spread out in a uniform layer over the earth, the depth would be about 10,000 ft. Water is closely associated with the processes of life; where water is absent or is present only in small amounts, the earth is a desert.

Physical Properties · At ordinary temperatures pure water is a clear, transparent liquid. It has a slightly bluish color, but this is only noticeable in water of considerable depth, especially in lakes in which the water is fairly pure. By definition it solidifies at 0° and boils at 100° under the normal pressure of the atmosphere at sea level. At higher elevations the pressure is less and the boiling point correspondingly lower. Thus, at Mexico City (elevation 7000 ft) water boils at 93°, while on the top of Mt. Everest (elevation 29,000 ft) it would boil at 71°.

Some of the properties of water are, from a chemist's point of view, remarkable.

1. **The specific heat of water is greater than the specific heat of any other common substance.** By the "specific heat" of a substance we mean the quantity of heat, measured in calories, required to raise the temperature of 1 g of the substance 1° C. The following table shows the specific heats of some common substances, for comparison:

SPECIFIC HEATS OF SOME COMMON SUBSTANCES (AT ROOM TEMPERATURE)

	CALORIES		CALORIES
Water	1.000	Copper	0.092
Oxygen gas	0.0156	Limestone ($CaCO_3$)	0.196
Iron	0.103	Sand (SiO_2)	0.188
Aluminum	0.212		

The specific heat of water is much larger than that of the metals or the rocks. Large bodies of water warm up only slowly when exposed to the sun's rays and cool down only slowly at night, while the sands of the desert or materials such as those used in paving streets or in the construction of buildings sometimes get hot enough to "fry an egg." Plant and animal tissues, which contain 70–90 per cent water, are better able to maintain their temperature within certain limits because of the high specific heat of water.

2. **The heat of vaporization of water—that is, the heat required to evaporate 1 g—is exceptionally high.** The following table shows water compared with some other liquids in this respect:

HEATS OF VAPORIZATION OF SOME LIQUIDS AT THEIR BOILING POINTS

	CAL/G		CAL/G
Water	539	Mercury	71
Alcohol	204	Kerosene	67
Ether	83	Lubricating oil	45

It is a well-known fact that the presence of large bodies of water influences climate. It does this, in part, by the cooling effect of evaporation. Hot winds blowing over the ocean, or even over the moist earth, are cooled; that is, some of their heat is absorbed by the water, about 590 cal of heat (at 10° C, the average temperature) for every gram of water that is evaporated. Also, the evaporation of water from the skin cools the surface of our bodies and is involved in the physiological mechanism by which our body temperature is kept constant, even when the temperature of the surrounding air is higher; and the evaporation of water from the leaves of trees cools the neighboring air.

3. **The density of water is greatest at 4°.** An increase in temperature above 4° causes expansion of liquid water, and a decrease in temperature below 4° also causes expansion (see the table below). As every student of physical geography well knows, a consequence of this is that when a body of water is chilled, in the winter, down toward a temperature of 4°, the denser surface water sinks, forcing the warmer water below to rise to the top, and thus tending to delay the formation of a crust of ice over the surface.

DENSITY OF WATER AT VARIOUS TEMPERATURES

TEMPERATURE	DENSITY	TEMPERATURE	DENSITY
0° (ice)	0.917	40°	0.9923
0°	0.9998	60°	0.9833
4°	1.0000	80°	0.9719
10°	0.9997	100°	0.9586
20°	0.9982		

4. **The density of ice is less than that of liquid water (see the table above).** In other words, water occupies a larger volume in the solid state. This is indeed exceptional behavior. All known substances, with a very few exceptions, have a greater density as solids than as liquids. Surface ice, if ice were denser than water, would settle to the bottom, and any

large body of water would become a block of ice with a puddle of water at the top, the puddle increasing in size in summer and decreasing in winter. Instead, because of this unusual property, the ice which forms remains on the surface and, to an extent, insulates the water below, thereby protecting the organisms which live there.

One of the potent weathering agencies is the expansion of water as it freezes to ice in the fissures and minute crevices of rocks, thereby breaking pieces off and effectively pulverizing the rocks.

5. **The heat of solidification (and of melting) of water is 80 cal/g.** Therefore 80 cal of heat is given off when 1 g of water freezes. The heat removed from freezing water in the soil and in lakes and rivers exerts a moderating effect in cold weather.

6. **Water is an excellent solvent.** Water is an especially good solvent for many electrovalent compounds and for some covalent compounds. One reason is that water has the high dielectric constant, 80. This means that, in water, the attractive force between oppositely charged particles (+ and −), such as *ions*, is greatly diminished; and they do not so easily aggregate to form insoluble clusters or crystals. Water is a medium in which many chemical reactions can take place, such as those that occur in the blood and other body fluids of animals and in the sap of plants.

The Composition of Natural Waters · All natural waters contain small amounts of mineral matter, either in solution or held in suspension. Even the water which falls to the earth in the form of rain contains particles of dust, as well as small quantities of gases absorbed from the atmosphere. Upon reaching the earth's surface it dissolves mineral matter present in the rocks and soil, such as common salt and compounds of calcium, magnesium, and iron. Waters containing such substances in solution are commonly spoken of as *hard waters* or, if large amounts of mineral matter are present, as *mineral waters*. The quantity and nature of the substances present vary with the nature of the rocks and soil with which the water comes in contact. The weight of such matter present in 1 liter of average well water varies from 0.1 to 0.5 g. Much larger quantities are present in the waters from some springs and very deep wells. The water of the ocean contains over 3.5 per cent of mineral matter, more than three fourths of which is common salt.

The water of the Great Salt Lake in Utah contains 23 per cent of solids, and that of the Dead Sea rather more. Large quantities of sodium chloride, bromine, and other useful substances are obtained by processing the water from oceans, salt lakes, and underground brines.

In addition to mineral substances, natural waters contain more or less organic matter. This consists not only of inanimate matter, derived from

SALTS IN AVERAGE DRY RESIDUE FROM EVAPORATED SEA WATER

COMPOUND	FORMULA	AVERAGE PERCENTAGE
Sodium chloride	NaCl	77.76
Magnesium chloride	$MgCl_2$	10.88
Magnesium sulfate	$MgSO_4$	4.74
Calcium sulfate	$CaSO_4$	3.60
Potassium sulfate	K_2SO_4	2.46
Magnesium bromide	$MgBr_2$	0.22
Calcium carbonate	$CaCO_3$	0.34
		100.00

the decay of organic substances on the earth's surface or present in sewage, but also of certain forms of living microorganisms (bacteria) which usually accompany such products. Waters taken from shallow wells or streams in thickly populated districts are likely to contain considerable quantities of such matter.

Pure Water for Chemical Uses · For many purposes, and especially for laboratory uses, it is necessary to have pure water. This is obtained by removing the foreign matter from natural waters by the process of *distillation* (Fig. 8-6). With rare exceptions the foreign matter in natural water is nonvolatile; hence, if such water is boiled in a suitable vessel, the water passes off in the form of steam and may be condensed, while the impurities remain in the vessel. Water purified in this way is called *distilled water* and is sufficiently pure for nearly all purposes.

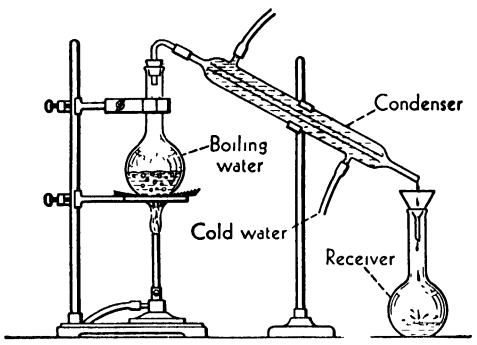


Fig. 8-6. Laboratory Distillation of Water

Chemical Properties · A knowledge of the chemical properties of water is of fundamental importance for an understanding of many chemical processes. The main topics to be considered under this head are the effect of heat upon water, the reaction between water and certain elements and compounds, and the part that water plays in promoting chemical changes.

1. **The effect of heat upon water.** We have seen that in the formation of water from hydrogen and oxygen a great deal of heat is liberated (p. 93). The law of conservation of energy tells us that an equal amount of energy in some form will be required to decompose water. This may be supplied by the electric current, which, as we have seen, will effect the

electrolysis of water. Heat alone will decompose it, although only to a slight extent even at very high temperatures. Compounds which are not readily decomposed by heat, such as water, are called *stable compounds.* The following table by Langmuir gives the percentages of the total quantity of water decomposed when heated in a closed system to the temperatures indicated. The results must be considered as approximate only, since the experiments are very difficult to carry out.

DECOMPOSITION OF WATER AT VARIOUS TEMPERATURES

TEMPERATURE	PERCENTAGE OF WATER DECOMPOSED	TEMPERATURE	PERCENTAGE OF WATER DECOMPOSED
1327°	0.0446	1727°	0.504
1427°	0.0920	1927°	1.21
1527°	0.17	2227°	3.38
1627°	0.302	2728°	11.10

Decomposition of Water by Heat Reversible · When water is heated in a closed vessel to a temperature above the point at which perceptible decomposition begins, the percentage of the total vapor decomposed gradually increases with the rise in temperature. If, however, the temperature is maintained constant at any point, the decomposition *apparently* ceases. In reality it continues, but the oxygen and hydrogen formed combine again and at such a rate that the quantity of vapor decomposed in a given time is exactly equal to that formed by the union of the oxygen and hydrogen. In other words, the vapor is in equilibrium with its decomposition products, namely, oxygen and hydrogen. The change, therefore, like the change of oxygen into ozone, is a reversible one and may be expressed as follows:

$$\underset{\text{water vapor}}{2\,H_2O} \rightleftarrows \underset{\text{hydrogen}}{2\,H_2} + \underset{\text{oxygen}}{O_2}$$

2. **The action of water as an oxidizing agent.** Since water contains 88.81 per cent of oxygen, we might expect it to be a good oxidizing agent; but in general this is not the case. Stable bodies are not reactive, and the great stability of water prevents its parting with oxygen, save to powerful reducing agents. Some of the metals are oxidized by very hot steam, as we have seen to be true in the case of iron (p. 86). In a similar way red-hot carbon is oxidized by steam in the production of hydrogen by the Bosch process (p. 89):

$$\underset{\text{carbon}}{C} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{carbon monoxide}}{CO} + \underset{\text{hydrogen}}{H_2}$$

3. **The action of water upon oxides.** Water combines with many of the oxides to form important compounds. It is convenient to divide these oxides into two general classes, according to the nature of the resulting

compounds: (1) *acidic oxides*, which combine with water to form *acids*, and (2) *basic oxides*, which combine with water to form *bases* (pp. 52–53).

4. The action of water in the formation of hydrates. Many compounds other than oxides, especially those called salts, combine with water to form definite compounds. For example, calcium chloride crystallizes from water as a compound which has the formula $CaCl_2 \cdot 6\ H_2O$, in which each calcium ion is combined with six molecules of water. The raised period between the two simple formulas signifies that the two kinds of compounds, $CaCl_2$ and H_2O, are chemically combined in the stated ratio. The crystals of blue vitriol, or bluestone, are composed of the compounds copper sulfate ($CuSO_4$) and water combined in the ratio of one to five, giving the compound $CuSO_4 \cdot 5\ H_2O$. When crystals such as these are heated, the water is driven off, but is regained when the salts are again exposed to water. Thus, the calcium chloride used for drying gases is $CaCl_2$, and exerts its drying action by reacting with the water vapor contained in the gases which are passed over it.

Such salts, before recombining with the water, are said to be *anhydrous*, while the compounds formed by their union with water are called *hydrates* Thus, blue vitriol is a *hydrate* of copper sulfate, while the white residue formed on heating this hydrate is *anhydrous* copper sulfate. Many anhydrous substances form two or more different hydrates by combining with different percentages of water. The water which combines with compounds to form hydrates is termed *water of hydration*, or sometimes *water of crystallization*, because many hydrates are crystalline in character and, when heated, lose water, with an accompanying loss of their original crystalline structure. Compounds crystallized from water are usually hydrated.

It should not be inferred that all crystalline substances contain water of crystallization. The majority of minerals, such as quartz and diamond, are crystalline without having water of crystallization. Likewise some salts, such as sodium chloride, at room temperature crystallize from water in the anhydrous form.

5. The action of water in promoting chemical changes. Many substances which have no action upon each other in the absence of water readily enter into combination in its presence. The reason for this is not always clear. In some cases the increased activity seems to be due entirely to the fact that when in solution the substances are brought into more intimate contact. On the other hand, all electrovalent compounds dissolved in water exist wholly or in part as free ions, and owe their great activity to these ions. Moisture also has a definite *catalytic* effect. Even a trace of water often has a marked influence in increasing the speed of certain chemical changes.

Methods for Finding the Exact Composition of Water · Many very careful experiments have been made for the purpose of determining, with as great accuracy as possible, the ratio in which hydrogen and oxygen are present in water; and it is worth our while to study somewhat in detail the methods which have been employed, since they illustrate in a striking way the types of procedure that are used in determining the composition of all compounds.

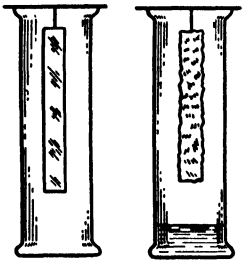


Fig. 8-7. Catalytic Effect of Water in Promoting the Oxidation of Iron · The strip of iron in the left-hand jar was kept in dry air. No oxidation took place. The air in the right-hand jar was moist and the iron was oxidized rapidly

Two *general* methods are available for such a purpose: first, *the method of analysis*, in which a given weight of the compound is separated either directly or indirectly into its constituent elements and the identity and weight of each determined; second, *the method of synthesis*, which consists in finding the proportion in which the constituent elements unite to form the compound, and which is therefore just the reverse of analysis.

Composition of Water by Analysis · It will be recalled that water may be decomposed easily into its constituents by the electric current. It would be expected that the exact composition of water could easily be found in this way, since the volumes of the gases liberated can be measured with accuracy; and, if we know their densities, the weights of the gases can be calculated. When the experiment is carried out, however, the results obtained are not concordant; in general, the volume of the hydrogen liberated is slightly more than double the volume of the oxygen. Experiments prove that the method is subject to several sources of error. For example, a portion of the oxygen liberated is converted into ozone; and the water through which the liberated gases bubble (Fig. 3-1, p. 22) dissolves more oxygen than hydrogen. The ratio between the weights of hydrogen and oxygen obtained in this process, therefore, does not represent with great accuracy the ratio in which they are combined in water. More accurate results are obtained by a number of synthetic methods, such as the one now to be described.

Composition of Water by Synthesis · In the synthetic methods we measure directly the quantities of oxygen and hydrogen which combine to form water; or we may determine the quantity of either of the elements which enters into the combination and then the weight of the resulting water. The difference between these two weights is equal to the weight of the other element. The greatest accuracy is obtained when all three of the substances involved are weighed directly.

Synthesis of Water by Morley · The method used by Morley (Fig. 8-8) consists in weighing pure hydrogen and oxygen, as well as the water resulting from their combination.



Science Service

Fig. 8-8. Edward Williams Morley (1838–1923) From 1869 to his retirement in 1906, professor of chemistry in Western Reserve University. Known for his accurate determination of the densities of hydrogen and oxygen, and of the ratio in which they combine to form water; associated with A. A. Michelson in his classic researches on the relative motion of ether and matter and the determination of the length of the meter in terms of the wave length of light; president of the American Association for the Advancement of Science (1895) and of the American Chemical Society (1899); recipient of many honors

As the average of twelve experiments Morley found that the *proportion in which hydrogen and oxygen unite to form water is as follows: by weight, 1 part of hydrogen to 7.94 parts of oxygen (or 1.008 parts of hydrogen to 8.000 parts of oxygen)*. Thus, Morley's results showed that the composition of water, expressed in percentages, is hydrogen, 11.19 per cent; oxygen, 88.81 per cent.

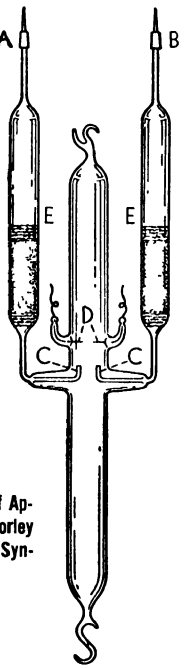


Fig. 8-9. Diagram of Apparatus Used by Morley for the Quantitative Synthesis of Water

Experimental Details · Fig. 8-9 represents the form of apparatus used by Morley for effecting the combination of hydrogen and oxygen and for weighing the resulting water. Extraordinary precautions were taken to ensure pure materials and to eliminate all known sources of error. The air was first removed from the apparatus, which was then sealed and weighed. A tube containing hydrogen absorbed in palladium (the hydrogen is released on heating) was weighed and joined to the apparatus at *A*, while a large globe filled with oxygen was weighed and connected at *B*. The two gases were then admitted to the apparatus through the tubes *C*, *C*, and their union effected as they entered by electric sparks passed between the points at *D*. In order that the resulting steam might be condensed as fast as formed, the apparatus was immersed in cold

water during the experiment. After from 30 to 35 g of water had been formed in this manner, the vessels from which the hydrogen and oxygen were supplied were disconnected and again weighed to determine the exact weights of hydrogen and oxygen admitted to the apparatus. There still remained in the apparatus, however, a certain amount of uncombined hydrogen and oxygen, which had to be measured. To do this the entire apparatus was immersed in a freezing mixture until the water which had been formed by the union of the hydrogen and oxygen was frozen. The mixture of the uncombined gases was then withdrawn through *A* and *B*. Any moisture present in the mixture was removed as the gas passed through the tubes *E*, *E*, which were filled with phosphorus pentoxide, a substance which has a strong affinity for water. The weights of hydrogen and oxygen present in the mixture were then found by analysis. Finally the apparatus itself was weighed to measure the increase in weight due to the water formed in the experiment.

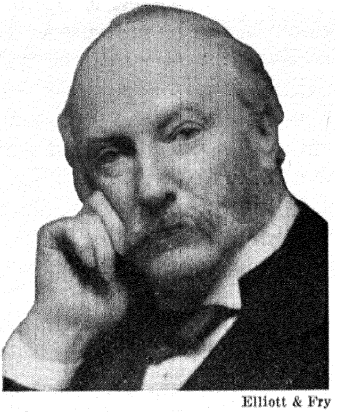
Comparison of Results Obtained · From the description of these methods it is easy to see that experiment alone can determine the composition of a compound. Different methods will sometimes lead to slightly different values. The more reliable the method chosen, and the greater the skill with which the experiment is carried out, the more accurate will be the results. It is universally conceded that Morley's results are the most trustworthy yet obtained.

The Rare Gases: Helium, Neon, Argon, Krypton, Xenon

Because of the minute percentages of these elements in the atmosphere, and also because of the similarity in properties between them and nitrogen, they were not discovered until comparatively recent years. They are colorless, odorless, tasteless gases and very difficult to liquefy. *They are characterized by their chemical inertness.* Although they have been subjected to the action of many other substances under conditions which have been most favorable for effecting the combination of elements, no one has yet succeeded in preparing any compounds of these elements (with the possible exception of an unstable chloride of krypton, unstable hydrates of argon, krypton, and xenon, and the unstable compounds of argon with boron trifluoride).

Historical · **Argon.** The first evidence for the existence of the inert gases in the atmosphere was obtained by Cavendish. In 1785, in the course of his experiments on air, he passed electric sparks through an enclosed volume of air (nitrogen and oxygen), introducing more oxygen from time to time, so as to make

certain that the quantity of oxygen present should be sufficient to combine with all the nitrogen. After repeated sparking, the oxides of nitrogen formed by the union of the gases, together with the excess of oxygen, were removed by absorbing them in appropriate liquids. In this experiment Cavendish observed that



Elliott & Fry

Fig. 8-10. Lord Rayleigh (John William Strutt) (1842–1919) Cavendish Professor of Physics at Cambridge University, and professor of natural philosophy at the Royal Institution of Great Britain. An accomplished investigator along many lines of physical research. His interest in Prout's hypothesis led him to study gas densities and to detect the difference in density between nitrogen from air and nitrogen from chemical sources. These studies, with Ramsay, resulted in the discovery of argon. He received the Nobel prize in 1904.

even after repeated trials there always remained a small residue of gas, in volume about $\frac{1}{120}$ of the air taken, which would not combine with oxygen and therefore presumably was not nitrogen.

No attention was paid to this observation until 1892, when Lord Rayleigh (Fig. 8-10) observed that 1 liter of nitrogen prepared from its compounds was lighter by about 5 parts in 1000 than the same volume prepared from air. He repeated his experiments many times, always with the same results. Finally he and Sir William Ramsay (Fig. 8-11), working together, showed that there was indeed a residue of extremely inert gas in nitrogen from air. This gas was named *argon* ("lazy one") because of its inert character.

Helium. In 1889 the American chemist Hillebrand found that certain minerals containing the element uranium evolve a gas when heated. After a brief investigation he concluded that the gas so evolved was nitrogen. In 1895,



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Fig. 8-11. Sir William Ramsay (1852–1916) Eminent Scottish chemist; professor of chemistry in University College, London, until 1913, when he retired. Ramsay and Lord Rayleigh, working together, discovered argon in 1894. Together with Travers, Ramsay also discovered neon, krypton, and xenon, and was the first to show that helium is a constituent of the atmosphere. For these remarkable discoveries he was awarded the Nobel prize for chemistry in 1904.

shortly after the discovery of argon, the attention of Ramsay was called to this experiment, with the suggestion that argon might be present in the gas which Hillebrand had obtained. Ramsay repeated the experiment, obtained the gas, and studied its spectrum. Some of the lines of this spectrum corresponded to no known element on the earth. Strangely enough, they did correspond to some lines found by the French astronomer Janssen in 1868 in the spectrum of the corona of the sun and attributed by Lockyer to an unknown element, *helium*, in the atmosphere of the sun. Shortly after the identification of helium in the gases evolved on heating uranium minerals, Ramsay was able to obtain the gas in fairly pure state and study its properties. Since that time helium has been found to be a constituent of our own atmosphere, of the gases from certain springs, and of natural gas in certain regions of Texas and elsewhere.

Neon, krypton, and xenon. Following the discovery of argon and helium an exhaustive examination of various gases was made, especially of those obtained from minerals, in the hope that still other elements might be discovered. These investigations proved fruitless until finally directed to liquid air as a possible source of such unknown elements. Large quantities of liquid air were subjected to careful fractional distillation, and the different fractions examined with the spectroscope for the presence of unknown elements. By this method Ramsay and Travers, in 1898, succeeded in isolating three additional elements, which were named *neon*, *krypton*, and *xenon* ("new," "hidden," and "stranger").

In an effort to discover still other elements in air, Moore examined the gases, first from 19 tons and later from 100 tons of liquid air, but found no new elements.

Uses of the Rare Gases · (1) The use of helium in the inflation of balloons and other lighter-than-air craft is especially desirable because it will not burn. Helium is about twice as heavy as hydrogen, but has 92.6 per cent of the lifting power of hydrogen. The Federal government maintains a plant in Texas to recover large quantities of helium from natural gas. In the recovery process advantage is taken of the low boiling point of helium (− 268.9°). This gas, which in 1918 cost $2500 per cubic foot, is now prepared at only a few dollars per thousand cubic feet. (2) Workers in caissons and diving bells suffer from the "bends," a condition brought on by nitrogen which dissolves in the blood (in the lungs) at the high pressure. No harm is done if the affected person passes through a "decompression chamber"; but the nitrogen escapes as bubbles in the blood, which block circulation, if the transition from high to normal pressure is made too rapidly. An artificial atmosphere of oxygen and helium greatly lessens the danger because of the extremely low solubility of helium. (3) By evaporating liquid helium under reduced pressure, a temperature of − 272.3° has been reached. Still lower temperatures have been attained (to within about 0.001° of the absolute zero) by other physical methods which involve the use of liquid helium. (4) Neon signs

consist of glass tubes of the desired forms, containing neon gas, at reduced pressure, through which an electric discharge passes. Sometimes a certain percentage of argon or helium (or both) is added to give a different color; and sometimes mercury is also introduced. (5) Argon is now extensively used in gas-filled electric filament lamps, which are more efficient than the older type filled with nitrogen.

SOME PROPERTIES OF THE RARE GASES

	HELIUM	NEON	ARGON	KRYPTON	XENON
Weight of 1 liter in grams .	0.1785	0.900	1.782	3.708	5.851
Weight of 22.4 liters . .	4.0	20.2	39.9	83.1	131.1
Atomic weight	4.003	20.183	39.944	83.7	131.3
Number of atoms per molecule	1	1	1	1	1
Number of cubic centimeters dissolved by 1 liter of water at 20° and 760 mm pressure	13.8	14.7	37.9	73.	110.9
Boiling point of liquid form	− 268.9°	− 246.3°	− 185.8°	− 152.9°	− 107.1°
Melting point of solid form	− 272.2°	− 248.67°	− 189.2°	− 169.0°	− 140°

The Spectroscope; Spectra of the Elements

The Spectroscope as a Chemical Tool · We have just noted that Rayleigh, Ramsay, and Travers were able to identify the rare gases of the atmosphere, including helium, through spectroscopic examination (see color plate); and in Chapter 17 (p. 303) we shall refer to Bunsen's study of the spectra of rubidium and cesium. Every element produces light of a characteristic wave length; the spectra of the elements are their "fingerprints." No two elements give the same spectrum, but the spectrum of each element is always the same (under the same conditions); hence the elements may be identified by their spectra.

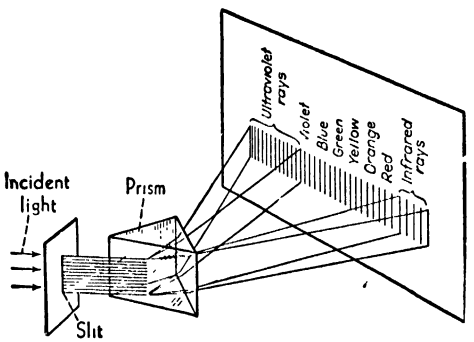


Fig. 8-12. The Separation of White Light into Its Constituents

Formation of the Spectrum · When a beam of light passes through a triangular prism of glass, it is bent out of its course and emerges at a decided angle with its original direction, as shown in Fig. 8-12. Ordinary light is made up of waves of many different lengths, and each one is bent, or *refracted*, to a different degree, so that the various colors corresponding to the different wave lengths are spread out in a *spectrum* (Fig. 8-12). The red is the least refracted, the violet the most.

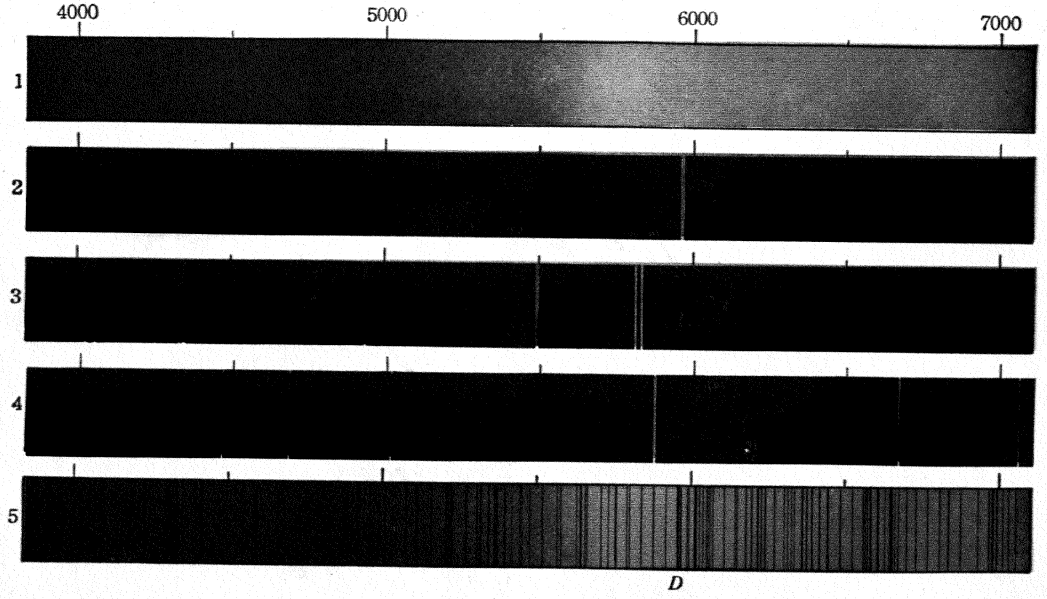


Fig. 8-13. Different Types of Spectra* · 1. Continuous spectrum from an incandescent solid. 2. Bright-line spectrum of sodium. 3. Bright-line spectrum of mercury. 4. Bright-line spectrum of helium. 5. Absorption spectrum of the sun, showing some of the strongest Fraunhofer lines. Note the coincidence of the bright lines for sodium in 2 and the dark lines *D* in 5

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A beam of *white* light from an incandescent solid gives a *continuous spectrum* of colors from red through orange, yellow, green, blue, to violet (see color plate of spectra facing page 122). The spectrum of any *colored* light is not necessarily continuous, but shows merely those colors of which the light is composed.

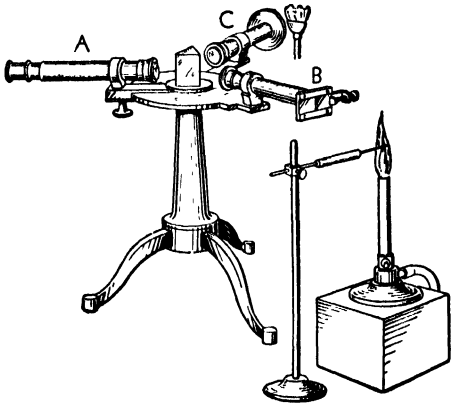
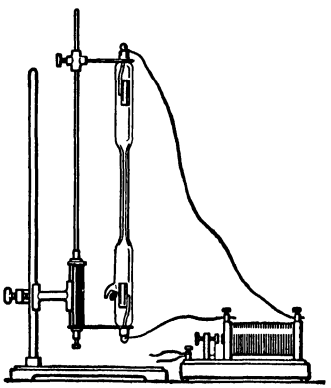


Fig. 8-14. Diagram of a Simple Spectroscope

Fig. 8-14 represents a spectroscope, an instrument invented by Bunsen and Kirchhoff in 1860 for viewing a spectrum. If we allow light, say from a colored flame, to enter the slit, *B*, and if we look into the eyepiece of the telescope, *A*, the spectrum of the flame is seen as a series of bright lines (images of the slit, *B*). The lines are seen against the background of a wave-length scale in *C*, which is visible to the eye at the same time.

Emission Spectra · A glowing gas or vapor gives an interrupted, or *brightline*, spectrum, as a rule characteristic of the *elements* present rather than of any compound. Even a slightly volatile solid, if heated sufficiently in a flame or spark, can be brought to a point where its vapor will emit light. A simple way to produce a *flame spectrum* is to dip a platinum wire into some of the substance or a concentrated solution of it, and heat it in a Bunsen flame. The flame takes on the color of the glowing vapor of the substance. When a higher temperature is desired, a little cavity may be hollowed out in the lower carbon of an arc light, and some of the substance placed in this. A so-called *arc spectrum* is then obtained. Metallic substances may be made to form a spark gap for an induction-coil discharge, to give a *spark spectrum*. Or, when a gas, such as neon gas, at a suitable low pressure is sealed within a tube provided with electrodes (Fig. 8-15) and excited with an electric discharge from an induction coil, or transformer, the gas becomes brilliantly luminous.


Fig. 8–15. Plucker Tube for Showing Vacuum-Tube Spectra

All these methods for producing spectra are extensively employed in analytical procedure, for identification of elements, and for the detection of elements which may be present in a given sample of material in extremely minute traces. Several of the elements have been discovered by finding spectral lines which had not previously been identified as characteristic of any known element.

Absorption Spectra · It has been previously stated that an incandescent solid gives a continuous spectrum. If a layer of gas is interposed between the incan-

descent solid and the prism, the gas will absorb those wave lengths of light which it can itself give out when luminous, and the continuous spectrum will be interrupted by a series of *black* lines corresponding to the bright lines of the gas. These black lines are known as *absorption lines*, and a spectrum in which they appear is called an *absorption spectrum*. In this way the solar spectrum is crossed by a great number of dark lines due to the presence of gases in the envelope surrounding the incandescent center of the sun. The absorption lines in the solar spectrum are called *Fraunhofer lines*, after their discoverer. We have learned much about the elements present in the sun's atmosphere from a study of its absorption spectrum.

Liquids, solids, and solutions also give absorption spectra, and their study has yielded much important information about the chemical structure of the molecules absorbing the light.

Spectra and Atomic Structure · From the pattern of the lines in the spectrum of an element it is possible to deduce the various energy levels of the electrons in the outer region of the atom. The manner of making this deduction will be discussed in Chapter 19.

QUESTIONS

1. What is the relationship between barometric pressure and the weight of the atmosphere?

2. (*a*) Cite evidence to prove that air is a mixture. (*b*) Indicate in schematic form, and by means of equations where possible, how you would proceed to remove the various constituents from a sample of air.

3. (*a*) Of what use is liquid air? (*b*) What are the chief commercial uses of nitrogen? (*c*) List some industrial uses of carbon dioxide.

4. (*a*) Name the constituents of the atmosphere that are essential for life. (*b*) Indicate the reasons why they are essential.

5. What would happen to life on this earth if the concentration of oxygen in the earth's atmosphere (*a*) were reduced to 10 per cent? (*b*) were increased, say, to 50 per cent?

6. Why does not the atmosphere, which is a gas, diffuse off into interstellar space, since diffusion is one of the properties of gases?

7. (*a*) Why is nitrogen chemically semi-inert? (*b*) Why are the rare gases inert?

8. Name some physical constants that are defined in terms of properties of water.

9. Water freezes at 0°, expands when it freezes, has a relatively high specific heat and heat of vaporization, and is a good solvent. Discuss these properties of water and their importance to life.

10. (*a*) What is the photosynthesis process? (*b*) In what various ways is it of importance to mankind?

PROBLEMS

1. A balloon of 100 liters capacity is anchored in the air under standard conditions. (*a*) Calculate the lifting force (measured in grams) if the balloon is filled with helium gas. (*b*) What would be the lifting force of the same balloon filled with hydrogen gas? (See the Appendix for liter-densities of the gases.) (*c*) Why is helium preferred to hydrogen for the inflation of balloons?

2. An aqueous solution of ammonia has a density of 0.898 g/ml, and contains 28 per cent by weight of ammonia (NH_3). Calculate the number of grams of ammonia in 1 liter of this solution.

3. In the formation of sugar ($C_6H_{12}O_6$) in photosynthesis, about 3.7 kcal of energy is stored for every gram of sugar formed. If we reverse the reaction, how much heat will be liberated by burning 100 lb of sugar in oxygen?

4. From the volumes of nitrogen and oxygen (measured at standard conditions) that dissolve in 100 ml of water at 0°, calculate the *weights* of the two gases that dissolve.

5. Calculate the amount of heat required (*a*) to melt 125 g of ice at 0°; (*b*) to raise the temperature of the water thus formed to 100°; (*c*) to vaporize the water at 100°.

6. The percentage by weight of moisture in a sample of air was determined by passing the air through a tube filled with calcium chloride (which removed all the moisture). Calculate the percentage from the following data:

Weight of air passed through the tube	16.2331 g
Weight of tube and contents (calcium chloride) at beginning of experiment	33.4652 g
Weight of tube and contents at end of experiment	33.6532 g

7. Twenty liters of dried air, measured at 16° and 740 mm pressure, was passed through a tube containing soda lime (p. 102) to remove the carbon dioxide. Calculate from the following data the number of volumes of carbon dioxide present in 10,000 volumes of the dry air:

Weight of tube and contents (soda lime) at beginning of experiment	28.1323 g
Weight of tube and contents at end of experiment	28.1451 g

8. Morley found the composition of water by determining the weights of hydrogen and oxygen that combine with each other to form water. The results of four trials were as follows:

HYDROGEN USED	OXYGEN USED	HYDROGEN USED	OXYGEN USED
(1) 3.2645 g	25.9176 g	(3) 3.8193 g	30.3210 g
(2) 3.2559 g	25.8531 g	(4) 3.8450 g	30.5294 g

In each case calculate the ratio in which the hydrogen and oxygen combined to form water.

CHAPTER 9

LAWS OF CHEMICAL COMBINATION; ATOMIC THEORY; ATOMIC AND MOLECULAR WEIGHTS; ISOTOPES

Introduction · In this chapter we shall return to a discussion of atoms and molecules. We shall show how it is possible to find the weights of these particles, or rather their relative weights, called atomic weights and molecular weights. Probably nothing is more important to chemists than to know the relative weights of atoms and molecules.

One cannot, of course, devise a balance sensitive enough to weigh a single atom or molecule. Not only are these unit particles of matter too small to be weighed, but they are much too small even to be seen. Fortunately, the chemist is not so much interested in the actual weights of atoms and molecules as he is in knowing how much heavier one kind of atom or molecule is than another; that is, he is interested in the *relative weights* of the different kinds of atoms and molecules. There are two methods for determining the relative weights of atoms and molecules, the method of the chemist and the method of the physicist. The chemist's method is based primarily on a knowledge of the ratios by weight in which elements are combined in chemical compounds. The physicist's method makes use of observations on the deflection of charged atoms or molecules shooting through electric and magnetic fields.

In this chapter we shall describe both methods, presenting the chemist's method first, and following through the many threads of the historical development, which covered nearly the whole of the nineteenth century.

Historical Background for the Chemist's Method

The Composition of Compounds · Naturally chemists from the very beginnings of their science have been interested in the composition of compounds. They have systematically developed laboratory analytical techniques for the examination of compounds: *qualitative analysis* to determine *what* elements are present, and *quantitative analysis* to determine

how much of each element is present in the compound being studied; and chemists have learned how to use the *synthesis* of compounds from the elements to check their analytical results.

Let us take the compound *water* as an example. One can show qualitatively that water decomposes, on electrolysis (p. 22), into the two gaseous substances hydrogen and oxygen, which can be identified by characteristic properties. One can show *quantitatively*, by weighing the amount of water that is decomposed and the amount of the two gases produced, that 100 grams of water is composed of 11.19 grams of hydrogen and 88.81 grams of oxygen. This result is confirmed by the extremely accurate results of Morley (p. 118), showing by synthesis that the composition of water is 11.19 per cent hydrogen and 88.81 per cent oxygen, by weight.

The Relative Combining Weights of Hydrogen and Oxygen · Next, let us point out that chemists have found it to be much more convenient and significant to represent the composition of a compound by recording the weight of one of the elements combined with one part by weight of the other. For example, the weight ratio in the water molecule, 88.81 grams of oxygen to 11.19 grams of hydrogen, is the same as the ratio 7.94 grams of oxygen to 1 gram of hydrogen:

$$\frac{88.81}{11.19} = \frac{7.94}{1}$$

The ratio 7.94 to 1 is an experimental fact, accurately determined by actual measurement.

Now, if we let ourselves consider what would be the consequences of applying Dalton's atomic theory (p. 27) to this situation, we recognize that whatever composition a body of pure water may have, the many billions of billions of tiny molecules of water present will each individually have the same composition as the whole body of water. Thus in a single molecule of the compound water there are 1 part of hydrogen and 7.94 parts of oxygen by weight.

Dalton and some of his colleagues supposed that a molecule of water contained 1 atom of hydrogen and 1 atom of oxygen, thus: H–O; and if this were true, the relative weights of hydrogen atom and oxygen atom would necessarily be 1 and 7.94. However, let us suppose that Dalton was mistaken in his assumption, and that there are really 2 hydrogen atoms joined to an oxygen atom in the molecule of water, thus: H–O–H. There would then be 2 hydrogen atoms to make up the 1 part of hydrogen. The relative weights of all the oxygen and hydrogen atoms in the water molecule would still be 7.94 to 1, but the ratio of the weight of the atom

of oxygen to 1 atom of hydrogen would be 7.94 to $\frac{1}{2}$, or, if we prefer not to deal with fractions, 15.88 to 1.

Thus it is evident that the chemist cannot determine whether the relative weights of the hydrogen and oxygen atoms are in the ratio 1 : 7.94, or 1 : 15.88—unless he knows the answer to the question: What are the actual numbers or relative numbers of the atoms present? In other words, what is the formula of the compound? Chemists fumbled in confusion for many years before methods were found for determining formulas and atomic weights which made a coherent picture consistent with all the experimental facts.

Combining Weights · In the meantime, since there was always uncertainty about the formula, and hence about the atomic weight, chemists frequently contented themselves with reporting a *combining weight*, about which there was no uncertainty. At first this was chosen as the weight of an element which combines with 1 gram of hydrogen. As chemists continued the work of finding the composition of compounds of the various elements, it became apparent that oxygen, rather than hydrogen, would make a better standard for comparison. The main reason was that oxygen forms compounds with so many more of the elements than hydrogen does; in fact, oxygen forms compounds with all the elements except the inert gases.

The change to oxygen as the standard was finally made official in 1905; and in order to avoid the making of a very radical readjustment of the values that had already been obtained for the various elements on the basis of 1.000 for hydrogen, the combining weight for oxygen was changed merely from 7.94 to 8.000. The combining weight of an element is now defined as the weight of that element which will combine with 8.000 g of oxygen. The shift from 7.94 to 8.000 meant, of course, a proportionate increase in the combining weights of all the other elements. For hydrogen the shift was from 1.000 to 1.008.

Determination of Combining Weights

1. **Analysis of silver oxide.** Let us take silver oxide as an example for the determination of combining weight, using oxygen as the standard.

Silver oxide (say, 1.8552 g), if heated in a crucible (Fig. 9-1) to a moderately high temperature, decomposes completely to give a metallic silver bead weighing 1.7271 g. The quantity of oxygen liberated is then found by subtraction:

$$1.8552 \text{ g silver oxide} - 1.7271 \text{ g silver} = 0.1281 \text{ g oxygen.}$$

The composition of silver oxide, in terms of per cent of silver and per cent of oxygen, can then be calculated:

$$\frac{1.7271}{1.8552} \times 100 \text{ per cent} = 93.1 \text{ per cent silver.}$$

$$\frac{0.1281}{1.8552} \times 100 \text{ per cent} = 6.90 \text{ per cent oxygen.}$$

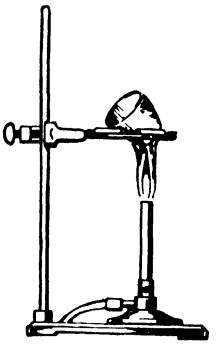


Fig. 9-1

Further, the combining weight of silver, x, is calculated as follows:

$$\frac{1.7271}{0.1281} = \frac{x}{8.000}$$

$$x = 107.88$$

This means that 107.88 g of silver combines with 8.000 g of oxygen.

2. **Synthesis of carbon dioxide.** A weighed quantity of carbon, purified with great care, is placed in a small porcelain boat (Fig. 9-2) and is heated to redness. Pure oxygen gas passes over it, unites with it to form carbon

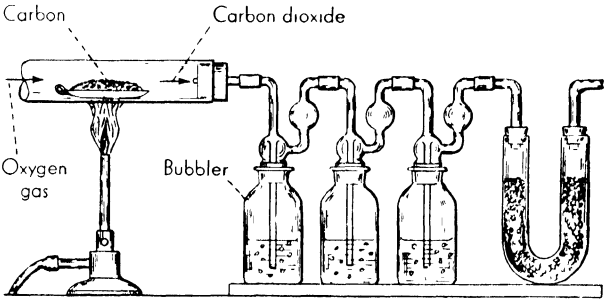


Fig 9-2. Apparatus for Determining the Composition of Carbon Dioxide

dioxide, and sweeps this into the bubbler bulbs, where the carbon dioxide reacts with a strong solution of potassium hydroxide and is retained in the solution as potassium carbonate (K_2CO_3). The U-tube, filled with anhydrous calcium chloride, catches and retains water vapor carried over from the bubblers. Therefore the increase in weight of the bubblers and the calcium chloride tube together is the weight of the carbon dioxide produced. In a typical synthesis of this sort, 0.0361 g of carbon unites with oxygen to give 0.1321 g of carbon dioxide. Consequently, the percentage of carbon in carbon dioxide is $\frac{0.0361}{0.1321} \times 100$ per cent = 27.3 per cent; and the percentage of oxygen is 100 per cent − 27.3 per cent = 72.7 per cent.

The combining weight of carbon is calculated from the equation:

$$\frac{72.7 \text{ per cent}}{8.000} = \frac{27.3 \text{ per cent}}{x}$$

$x = 3$. Three grams of carbon combine with 8.000 g of oxygen to form 11.00 g of carbon dioxide.

Combining Weights as Equivalent Weights · By experiments such as those above, the combining weights of many elements may be obtained. The values for four of them are tabulated below:

8.000 g oxygen combines with 1.008 g hydrogen.
8.000 g oxygen combines with 35.457 g chlorine.
8.000 g oxygen combines with 3.00 g carbon.
8.000 g oxygen combines with 107.88 g silver.

The four elements on the right combine not only with oxygen but also with each other. Determination of the composition of the compounds shows that

1.008 g hydrogen combines with 35.457 g chlorine.
1.008 g hydrogen combines with 3.00 g carbon.

and

35.457 g chlorine combines with 3.00 g carbon.
35.457 g chlorine combines with 107.88 g silver.

Silver is already listed as combining with oxygen and chlorine. It does not combine with hydrogen or carbon.

These combining weights, 8.000 g for oxygen, 1.008 g for hydrogen, 35.457 g for chlorine, 3.00 g for carbon, and 107.88 g for silver, and similar combining weights for the other elements, are also called equivalent weights. The reason for this is that chemical combination between these elements occurs in these weight ratios, as shown above. For example, 3 g of carbon combines with (is equivalent to) 8 g of oxygen, and with 1.008 g of hydrogen, and with 35.457 g of chlorine; and these weights of the last three elements combine with (are equivalent to) each other. Chemists use the terms *combining weights* and *equivalent weights* interchangeably; the terms mean the same thing.

Multiples of Combining Weights · Under certain conditions carbon will combine with oxygen in the ratio 6 : 8 (to form carbon monoxide) rather than in the ratio 3 : 8 (to form carbon dioxide). Union by multiples of combining weights, as well as by single combining weights, is not uncommon among the elements (pp. 26-29).

Law of Multiple Proportions · We mention some further cases. For example, 27.925 g of iron combines with 35.457 g of chlorine; also, 2×27.925 g of iron combines with 3×35.475 g of chlorine. In another

case 100.305 g of mercury combines with 8.000 g of oxygen; 2×100.305 g of mercury combines with 8.000 g of oxygen.

Another interesting illustration is to be found in the oxides of nitrogen. Nitrogen forms a series of oxides with an increasing proportion of oxygen (see the table below). If the weights of oxygen combining with a fixed weight of nitrogen, 2×7.004 g, are examined, they are found to be in the small-whole-number ratio $8 : 16 : 24 : 32 : 40 = (1 \times 8) : (2 \times 8) : (3 \times 8) : (4 \times 8) : (5 \times 8) = 1 : 2 : 3 : 4 : 5$.

OXIDES OF NITROGEN AND THE LAW OF MULTIPLE PROPORTIONS

OXIDE OF NITROGEN		PERCENTAGE COMPOSITION		COMBINING RATIO	
		Nitrogen	Oxygen	Nitrogen	Oxygen
Nitrous oxide	N_2O	63.65	36.35	2×7.004	8
Nitric oxide	NO	46.68	53.32	2×7.004	16
Nitrogen trioxide	N_2O_3	36.86	63.14	2×7.004	24
Nitrogen dioxide	NO_2	30.45	69.55	2×7.004	32
Nitrogen pentoxide	N_2O_5	25.94	74.06	2×7.004	40

Law of Combining Weights or Equivalent Weights · A study of many thousands of compounds of the various elements has shown that *all* the elements have combining weights, simple or multiple, just as do those elements listed in the last two pages. The *law of combining weights* may now be stated: *For every element we can determine by experiment a number, which, in itself, or when multiplied by some small whole number, 2, 3, 4, 5 . . . , expresses the weight by which the element enters into combination with other elements.* This law is one of the most convincing arguments for the existence of atoms; for how else, other than by combination of particles of fixed weight—that is, of atoms of fixed weight—could the existence of combining weights be explained?

Determination of Relative Weights of Atoms · The above discussion has shown the procedures by which the composition of compounds may be obtained, and the combining weights of the elements. But we have yet to answer the other question which, as pointed out at the beginning of this chapter in connection with the water molecule, must also be answered before the relative weights of atoms can be deduced, namely the question: *How many atoms are present in a molecule of the compound under consideration?* Is water HO, H_2O, or something else?

In the case of covalent compounds which can be studied in the gaseous state, such as water and hydrogen chloride, the answer is based on Gay-Lussac's *law of combining volumes.* For such compounds, the chemist succeeds in getting the answer to his question, because he is provided

with a scheme for collecting, or dealing with, equal numbers of different kinds of molecules.

Gay-Lussac's Law of Combining Volumes · When chemical reactions occur between solids or liquids, no general relationship exists between the volumes of products and reactants. When gaseous substances react, however, there is such a relationship, first observed and stated by the eminent French chemist Gay-Lussac in 1808: When two gases combine, there is a whole-number ratio between their volumes, and between the volume of either one of them and that of the product, if it too is a gas. It is to be understood that these volumes must be measured under the same conditions of temperature and pressure, since otherwise the volumes would change as a result of changes in these conditions.

For example, it can be shown experimentally that

2 volumes of hydrogen + 1 volume of oxygen produces 2 volumes of steam

and similarly, that

1 volume of hydrogen + 1 volume of chlorine produces 2 volumes of hydrogen chloride

In each of these cases all reactants and products are gases, and the whole-number ratios between their volumes are 2 : 1 : 2 and 1 : 1 : 2.

Avogadro's Law · How is this uniform behavior of combining gases to be explained? According to the atomic theory, chemical combination takes place between atoms in whole-number ratios; now we find that, for gases, combination takes place between volumes in whole-number ratios. What is more natural than to assume that equal volumes of gases contain equal numbers of atoms? That a ratio of atoms automatically becomes the same ratio of volumes? Avogadro clearly stated the correct principle in 1811: *Equal volumes of all gases under the same conditions of temperature and pressure contain equal numbers of molecules* (Avogadro's law, Chap. 6).

To many chemists, however, Avogadro's proposal had no meaning, for they failed to distinguish clearly between atoms and molecules. Dalton, for example, insisted that Gay-Lussac's experiments must be incorrect, for how could the union of an atom of hydrogen with an atom of chlorine produce *two* "atoms" of hydrogen chloride? An equally important contribution of Avogadro to the problem of atomic weight was his suggestion that the important free particle of a gas was the molecule, and that *molecules of even elementary gases might contain more than one atom.* This suggestion remained unnoticed for nearly half a century, until it was revived by Avogadro's countryman, Cannizzaro, and explained at a con-

gress of chemists called in 1860 to consider the confusing atom-and-molecule problem. The effect of Cannizzaro's explanation was such that Lothar Meyer, one of those present at the congress, wrote "It was as if the scales fell from my eyes. Doubt vanished, and was replaced by a feeling of peaceful clarity."

Interpretation of Gay-Lussac's Law · In the case of the reaction of hydrogen and chlorine, let us suppose that 1 tiny volume of hydrogen

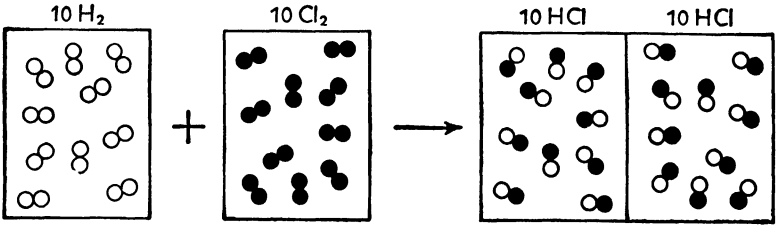


Fig. 9-3. Diagram Showing Volumes of Hydrogen and Chlorine Reacting and Volumes of Hydrogen Chloride Formed

contains 10 molecules. Then the 2 volumes of hydrogen chloride must each contain 10 molecules, or 20 all together (Avogadro's law). But each of these 20 molecules of hydrogen chloride must contain at least 1 atom of hydrogen, or 20 in all; and these 20 atoms came from 10 molecules of hydrogen. Consequently, each of the 10 original molecules of hydrogen must have contained at least 2 atoms; that is, the formula of the hydrogen molecule is probably H_2. A similar argument shows that the chlorine molecule contains at least 2 atoms, Cl_2. This reasoning does not permit us to say that these gases are diatomic; the molecules might each have contained 4 atoms (or some other simple multiple of 2 atoms).

However, the assumption that there are 2 atoms is the simplest explanation of the facts, and there is no evidence that hydrogen and chlorine molecules contain more than 2 atoms. As a matter of fact, other lines of reasoning, one based on measurements of specific heats of gases, and another based on X-ray studies of crystalline solids, combined with information from Gay-Lussac's law, show that many of the elementary gases, such as N_2, Br_2, I_2, or O_2, are diatomic.

The Formula for Water · The knowledge of the diatomic character of the hydrogen molecule permits us to deduce the formula for water from the combining ratios of hydrogen and oxygen. Here two volumes of hydrogen combine with one volume of oxygen to form two volumes of steam. If, again, a tiny volume of hydrogen contains 10 molecules (Fig. 9-4), then an equal volume of oxygen must contain 10 molecules, and the two volumes of steam must contain 20 molecules, by Avogadro's

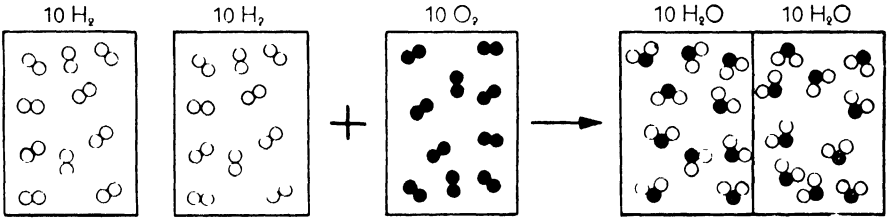


Fig. 9-4. Diagram Showing Volumes of Hydrogen and Oxygen Reacting and Volumes of Water Vapor Formed

law. The conclusion, then, is (1) that the oxygen molecule is diatomic, since 20 molecules of water, each containing 1 oxygen atom, are formed from 10 molecules of oxygen; and (2) that each water molecule must contain 2 hydrogen atoms, since the 40 atoms of hydrogen (in the 20 molecules of hydrogen) have appeared in 20 molecules of water. Thus the formula of water is H_2O.



Fig. 9-5 Stanislao Cannizzaro (1826–1910) Famous professor of chemistry at Palermo and Rome. Many of his researches were concerned with organic compounds. But he rendered his greatest service to chemistry by his interpretation and explanation of Avogadro's theories, and by his insistence on the distinction between atomic and molecular weights.

Having proved the formula of water to be H_2O, chemists were now able to obtain the ratio of the weight of a hydrogen atom to the weight of an oxygen atom. The *combining weight* ratio is 1.008 to 8.000, but since the atom ratio is 2 to 1, the *atomic weight* ratio is 0.504 to 8.000. It seemed desirable to avoid numbers less than one for atomic weights; hence these numbers were multiplied by two to give 1.008 as the atomic weight of hydrogen, 16.000 as the atomic weight of oxygen. The hydrogen atom, therefore, weights about one-sixteenth, or $\left(\frac{1.008}{16.000}\right)$, as much as an oxygen atom, and we define the *atomic weight of an element* as *the weight of an atom of that element relative to the weight of an oxygen atom taken as 16.000.* If the atomic weight is expressed in grams, it is called the gram-atomic weight. For example, the gram-atomic weight of oxygen is 16 grams; of carbon, 12.01 grams.

Atomic Weights of Solid Elements · The application of the laws of Gay-Lussac and of Avogadro would enable chemists to determine the formulas of gaseous compounds, and hence the atomic weights of the elements contained in them. What, however, is to be done about those elements, such as metals, which do not form easily studied gaseous compounds? The answer was found by Dulong and Petit in 1819, when they discovered that a measurement of the specific heat of metals or other solid elements gave them a method for counting out equal numbers of atoms of the elements, just as Avogadro's law gave a method for counting out equal numbers of molecules of gaseous substances.

Specific heat. The specific heat is numerically equal to the number of calories required to raise the temperature of 1 gram of substance 1° C. It may be determined by heating a known weight of the material whose specific heat is to be determined to a measured temperature, putting it into a measured quantity of water, and measuring the temperature to which the material and water finally come. The weight of water multiplied by its temperature rise will give the number of calories lost by the material. This quantity, divided by the drop in temperature of the material, will give the *heat capacity* of that particular weight of material, that is, the number of calories necessary to raise its temperature by 1°. Division of the heat capacity by the weight of material gives the specific heat.

Example. A piece of silver weighing 50 g, at a temperature of 100°, is put into 60 g of water at 25°. The final temperature of both silver and water is 28.4°.

$$\text{Calories gained by water} = 60 \times (28.4 - 25) = 204 \text{ cal.}$$

$$\text{Heat capacity of the piece of silver} = \frac{204}{100 - 28.4} = 2.85 \text{ cal. per degree.}$$

$$\text{Specific heat of silver} = \frac{2.85}{50} = 0.057 \text{ cal. per degree per g.}$$

Law of Dulong and Petit · Dulong and Petit observed that the product of the combining weight of an element by the specific heat of the element was close to 6.2, or some simple fraction, $\frac{1}{2}$ or $\frac{1}{3}$, of 6.2. They then made the bold generalization that, as far as the capacity of atoms to absorb heat was concerned, all atoms should be alike, regardless of their weight; hence those elements for which the product was less than 6.2 had atomic weights which were twice or three times their combining weights. Thus for all elements

$$\text{Atomic weight} \times \text{specific heat} = 6.2 \text{ cal. per degree.}$$

This equation applied to the solid element sulfur gives a result which agrees with the atomic weight of sulfur obtained from a study of its gaseous compounds; this agreement forms a bridge between the two methods, and shows them to be consistent with each other.

It is to be noted that Dulong and Petit's generalization means that the heat capacity of a solid element depends only upon the number of atoms present, and not upon their weight. Hence if one is dealing with a quantity of a solid element which requires 6.2 calories to raise its temperature 1° C, one has collected the total number of atoms of that element required to give the atomic weight in grams. It follows that if one divides the atomic heat, 6.2 calories per degree, by the specific heat (calories per degree per gram), one obtains the gram-atomic weight. Thus the gram-atomic weight of silver is $\frac{6.2}{0.057} = 108.7$. The resulting value will be only approximate, since the value 6.2 is only an average value.

An accurate value can be obtained by relating this approximate value to the combining weight, which can be exactly determined. The combining weight of silver is 107.88; this is close to the approximate atomic weight (108.7) and shows that the exact atomic weight is 107.88.

Molecular Weights and the Chemist's Method

The preceding historical discussion has shown the road which chemists took in formulating the atomic theory and establishing a firm basis for the choice of 16.000 for oxygen as the standard for atomic weights. It has also shown that the oxygen molecule is diatomic, with the formula O_2, and that the atomic heat of solid elements has the average value 6.2. With this as a background, we might ask. How would a chemist proceed today, if he were asked to determine, by chemical methods, the atomic weight of an element?

If the element was a solid at ordinary temperatures, he might well use the procedure of Dulong and Petit just described, and determine the approximate atomic weight from the specific heat and the exact atomic weight using the combining weight.

If the element formed gaseous compounds, however, he would more likely determine the molecular weight of several of the compounds, and relate these molecular weights to the composition of the compounds and combining weights in order to determine the exact atomic weight. Let us now describe methods by which the relative weights of molecules (molecular weights) may be determined experimentally.

Determination of Molecular Weight · The relative weights of molecules can be determined if we can find ways of obtaining *equal numbers of molecules*. The reasoning leading to this statement may be illustrated by the following analogy.

Suppose we were required to determine the relative weights of two sizes of lead shot (*A* and *B*, Fig. 9-6), and the balance available was accurate to only a fraction of an ounce. One shot would not move the balance enough to enable us to read the weight. We could, however, count out, say, 10,000 shot (*A*) and determine the weight. We could then count out 10,000 of the other size (*B*) and determine this weight. The ratio of the two weights is the same as the ratio of the weights of the individual shot.

$$\frac{\text{Weight of 10,000 } A}{\text{Weight of 10,000 } B} = \frac{10{,}000 \times (\text{weight of 1 } A)}{10{,}000 \times (\text{weight of 1 } B)} = \frac{\text{weight of 1 } A}{\text{weight of 1 } B}$$

Thus, if 10,000 *A* weighs 3 pounds and 10,000 *B* weighs 2 pounds, the weight ratio of *A* to *B* is 3 to 2. Notice that it is not even necessary to know that the number is 10,000 in each case; only that the number is the same in each case.

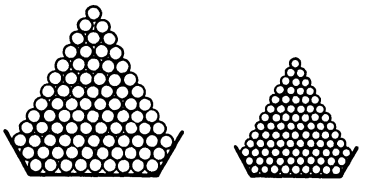


Fig. 9-6. Showing Equal Numbers of Shot of Different Sizes

In a similar way, in order to compare the weights of molecules of two substances it is only necessary to have equal numbers of the molecules of the two substances. There are several ways of obtaining equal numbers of molecules.

Methods of Collecting Equal Numbers of Molecules · We have seen (p. 80) that equal volumes of any two gases, under the same conditions of temperature and pressure, contain the same number of molecules (Avogadro's law). This gives an easy way of getting equal numbers of molecules of any two gaseous substances. If we compare the weights, for example, of one liter of oxygen and one liter of hydrogen, both at standard conditions, we are comparing the weights of equal numbers of molecules, and our ratio will be the same as the ratio of the weights of single molecules of the two gases. The weight of a liter of oxygen is 1.429 g; that of a liter of hydrogen is 0.08987 g.

The molecular weight of oxygen, on the basis of the oxygen atom as 16.000, is 32. The molecular weight of hydrogen gas is then determined from the proportion

$$\frac{1.429}{0.08987} = \frac{32}{x}$$

$$x = \frac{32 \times 0.08987}{1.429} \quad \text{or} \quad \frac{32}{1.429} \times 0.08987 = 2.012$$

The result is an approximate one because Avogadro's law, like the other gas laws, does not hold true exactly (p. 73).

Gram-Molecular Weights and the Gram-Molecular Volume · In all such calculations the fraction $\frac{32}{1.429}$ will appear, since the standard is oxygen. This fraction may be expressed in the decimal system as 22.4 and we reach the conclusion that 22.4 times the weight of one liter of any gas is its molecular weight expressed in grams.

The molecular weight of a compound, expressed in grams, is its *gram-molecular weight,* or *mole* for short. Thus the *gram-molecular weight* of oxygen is 32 grams. The volume occupied by the *gram-molecular weight* of a gas is called the *gram-molecular volume.* At standard conditions this is 22.4 liters.

The Avogadro Number · The number of molecules present in a gram-molecular weight is called the Avogadro number, in honor of the great Italian chemist, Amedeo Avogadro (p. 2). It is, of course, an enormous number—602,000,000,000,000,000,000,000, or 6.02×10^{23}, or 602 thousand billion billion. This number has been counted or calculated in half a dozen or more different ways. In Chapter 6, in connection with the spinthariscope, where we saw that atoms of helium are shot off from radium and produce visible flecks of light as they strike a zinc sulfide screen, it was stated that one can count the number of helium atoms that accumulate to give a tiny measurable volume, or weight, of helium gas. It is then easy to calculate the Avogadro number, the number of helium atoms present in the gram-molecular weight, 4.003 g, of helium. Lord Rutherford and two of his students in 1905 obtained a good value for the Avogadro number in this way.

Determination of Molecular Weights · The conclusion reached, in the second paragraph preceding, that "22.4 times the weight of a liter of a gas at standard conditions is the gram-molecular weight of the gas" can be turned around to read "the weight of 22.4 liters of the gas at standard conditions is its gram-molecular weight." This is the weight of an Avogadro-number's-worth of molecules. We can therefore go into our laboratory, measure out a volume of 22.4 liters of the gas in question, weigh it, and get the value for the gram-molecular weight and consequently also the molecular weight. Since 22.4 liters is too large a volume to handle conveniently on the pan of a chemical balance, we may measure the weight of any convenient volume of the gas or vapor under any convenient conditions of temperature and pressure. Then we calculate the weight of 22.4 liters under standard conditions. It is to be expected that molecular weights may be in error by a few per cent because, aside from experimental errors, there are deviations from the gas laws; and Avogadro's law itself is in error to the extent to which the gas laws fail.

Molecular Weights of Gases (Method of Dumas) · An experimental method for determining vapor densities, employed as early as 1827 by the French chemist Dumas, is readily adapted to the present purpose. A glass bulb, capacity about 100 ml, is attached to a vacuum pump, exhausted of the air which it contains, and weighed empty. The flask is then filled with the gas under investigation, and again weighed. If we know the volume of the flask, the weight of the gas which fills it, and the temperature and pressure under which it was filled, it is easy to calculate the weight of 22.4 liters of the gas under standard conditions. The method is also applicable to liquids that are easily vaporized. The liquid may be placed in the flask and the flask immersed in a bath the temperature of which is above the boiling point of the liquid (Fig. 9-7). The liquid rapidly boils away, drives out the air, and leaves the flask filled with the vapor of the liquid at the temperature of the bath and the pressure of the atmosphere. The flask may then be closed and its weight determined.

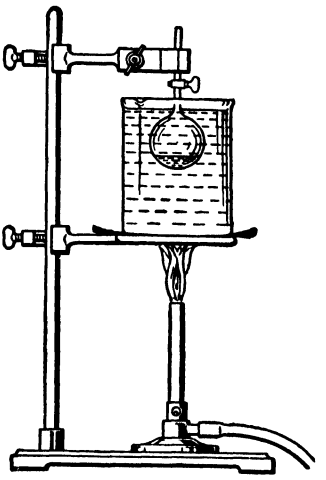


Fig. 9-7. Method of Dumas

Examples. 1. Suppose that a Dumas bulb of 90.7 ml volume is filled with ammonia gas at 0° and 760 mm, and that the ammonia is found to weigh 0.0688 g. What is the molecular weight of ammonia?

$$\frac{90.7 \text{ ml}}{22{,}400 \text{ ml}} = \frac{0.0688 \text{ g}}{x \text{ g}}; \quad x = 17 \text{ g, the gram-molecular weight.}$$

Hence the molecular weight of ammonia is 17.

2. Let us place about 20 ml of liquid water inside a Dumas bulb of 100 ml volume, boil off the water, and finally bring the bulb to a temperature of 110° in an oil bath just before we close off the bulb from the atmosphere (barometric reading is 752 mm). The weight of the water vapor is 0.0567 g. What is the molecular weight of water vapor?

Reduce the volume to standard conditions:

$$100 \text{ ml} \times \frac{752}{760} \times \frac{273}{383} = 70.5 \text{ ml}$$

$$\frac{70.5 \text{ ml}}{22{,}400 \text{ ml}} = \frac{0.0567 \text{ g}}{x \text{ g}}; \quad x = 18 \text{ g, the gram-molecular weight.}$$

Hence the molecular weight of water is 18.

It is of interest to point out that what we have done in the case of water is to calculate the weight which 22.4 liters of water vapor would have at standard

conditions, if we could obtain it as a gas at these conditions. Actually water is a liquid or a solid at 0° C.

Molecular Weights of Nonvolatile Covalent Compounds · Are there any methods other than that used for gases by means of which a known number of molecules may be counted out? It is found experimentally that the freezing point of a liquid is lowered when something is dissolved in the liquid; further, *the lowering of the freezing point of the solvent liquid is proportional to the number of molecules dissolved* in a definite amount of solvent. Equal freezing-point depressions, then, mean equal numbers of molecules dissolved, just as equal volumes of gases mean equal numbers of gas molecules. Measurement of the freezing-point lowering caused by a given weight of substance then permits us to measure the number of molecules in that weight; hence also the molecular weight. It is necessary to use a solution of a substance of known molecular weight to find out what lowering is produced by a known number of molecules. Any volatile liquid of which the molecular weight can be measured as a gaseous substance can be used for this purpose. Alcohol, for example, is such a substance; it is found that one mole of alcohol, 46 g, when dissolved in 1000 g of water, will lower the freezing point of water from 0° to − 1.86° C. The freezing-point depression found, 1.86°, was produced by dissolving 6.02×10^{23} alcohol molecules in 1000 g water; a weight of any other covalent substance which, when dissolved in 1000 g of water, lowers the freezing point by 1.86° must also contain 6.02×10^{23} molecules, and that weight will be its gram-molecular weight. The quantity "1.86° when in 1000 g of water" corresponds to the quantity "22.4 liters" in determining molecular weights of gases; it was obtained by using a substance of known molecular weight (alcohol, 46 g), just as 22.4 liters was obtained by using a substance of known molecular weight (oxygen, 32 g).

Every *solvent* has its own characteristic value for the freezing-point depression produced by dissolving one mole in 1000 g; for water it is 1.86°; for acetic acid, 3.9°; for benzene, 5.1°; for naphthalene, 6.3°.

Example. In an experiment 0.46 g of sugar, dissolved in 20.3 g of water, lowered the freezing point 0.126°. Calculate the molecular weight of sugar.

The available information gives the freezing-point lowering (1.86°) when 1000 g of water is used. The first step, then, is to convert from 20.3 g of water to 1000 g by solving the proportion

$$\frac{20.3 \text{ g}}{1000 \text{ g}} = \frac{0.46 \text{ g}}{x \text{ g}}; \quad x = 22.7 \text{ g}.$$

This gives the weight of sugar which, dissolved in 1000 g of water, would lower the freezing point 0.126°. A gram-molecular weight dissolved in

1000 g of water would lower the freezing point 1.86°; hence the gram-molecular weight is obtained from

$$\frac{1.86}{0.126} = \frac{x}{22.7}; \quad x = 337 \text{ g}.$$

Thus the molecular weight of sugar is 337.

Approximate Atomic Weights from Molecular Weights · Having now defined molecular weight, gram-molecular weight, gram-molecular volume, and Avogadro number, and having described two methods for determining molecular weights, one using gases and volatile compounds and the other nonvolatile compounds, we come finally to our objective, the extraction of atomic weights from molecular weights.

Procedure · Suppose we wish to determine the atomic weight of nitrogen, an element which forms a number of gaseous compounds, the molecular weights of which are easily determined. For each compound we determine the molecular weight and, by chemical analysis, the percentage of nitrogen in the compound. The values are shown in the table below.

If we multiply the weight of one liter of the gas at standard conditions by 22.4 we obtain the approximate molecular weight, based on the standard $O_2 = 32$. If we then multiply the molecular weight of each compound by the percentage of nitrogen, the product will give the fraction of the molecular weight which is due to the nitrogen present (last column). We do not know how many atoms of nitrogen these weights represent; we do know, from the atomic theory, that they represent the weights of one, two, three, or some higher whole number of nitrogen atoms. They could not be the weight of $1\frac{1}{2}$ nitrogen atoms, for example. In the table below, the weights of nitrogen are very near either to 14 or to twice 14. If we examine a large number of compounds in this way, it is reasonable to expect that we shall find some that contain only 1 atom of nitrogen; since we find none that give a weight less than 14, and since all other weights are multiples of 14, we conclude that 14 represents the atomic weight of nitrogen.

AMOUNT OF NITROGEN IN SOME NITROGEN COMPOUNDS

COMPOUND (OR ELEMENT)	PERCENTAGE OF NITROGEN BY ANALYSIS	WEIGHT OF ONE LITER AT STANDARD CONDITIONS	MOLECULAR WEIGHT (WT OF 22 4 LITERS IN GRAMS)	CALCULATION	PART OF MOLECULAR WEIGHT DUE TO NITROGEN
Nitrogen gas	100	1.2506 g	28.01	100% of 28.01 =	28.01
Nitrous oxide	63.65	1.9777 g	44.30	63.65% of 44.30 =	28.19
Nitric oxide .	46.68	1.3402 g	30.02	46.68% of 30.02 =	14.01
Ammonia . .	82.24	0.7707 g	17 26	82.24% of 17.26 =	14.19
Cyanogen . .	53.74	2.32 g	51.97	53.74% of 51.97 =	27.93

Exact Atomic Weights · Atomic weights determined as above are only as accurate as the molecular weights from which they were obtained. These, as has been shown (p. 138) are only approximate. Thus, from the table we can conclude that the approximate atomic weight of nitrogen is 14. The actual figures obtained are 14.01, 14.19, and $\frac{1}{2}$ of 28.01, 28.19, and 27.93. In order to determine the exact atomic weight we go back to the combining weight, just as in the application of the law of Dulong and Petit. Let us take, for example, the compound nitric oxide, the composition of which is 46.68% nitrogen and 53.32% oxygen. The combining weight of nitrogen is then calculated from the proportion

$$\frac{46.68}{53.32} = \frac{x}{8};\ x = 7.004.$$

Since this bears a simple numerical relationship to the atomic weight ($\frac{1}{2}$, $\frac{1}{3}$, etc.) it is clear that the atomic weight is exactly $2 \times 7.004 = 14.008$.

The Physicist's Method

The several forms of the chemist's method, which were the classic methods for atomic-weight determination, and which we have just been discussing, were employed throughout the course of nineteenth-century chemistry, and have been used even in recent times. In the 1920's a new tool, the Aston mass spectrometer, became available and has been developed into a very powerful instrument, of great precision, by means of which the weights of atoms can be compared with one another directly.

Principle of the Mass Spectrometer · The principle of the mass-spectrometer method is easily understood; it is the same as that of "winnowing." If one throws a handful of threshed wheat into the wind, the heavier wheat kernels fall almost directly down to the ground, but the lighter chaff is carried away by the wind, and falls at a distance from the kernels. This analogy can be made more definite in the following manner:

Suppose that we have a gun (Fig. 9-8) which fires bullets by the release

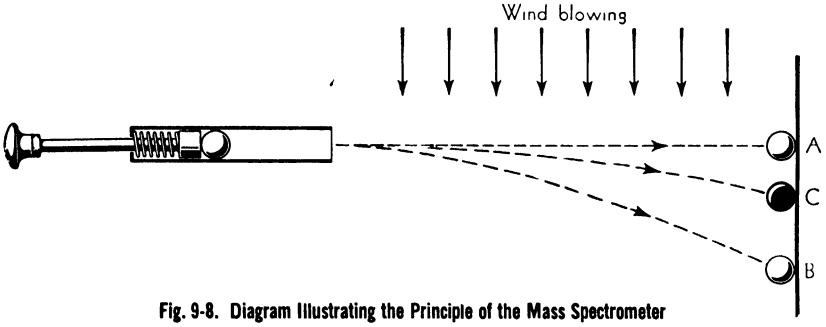


Fig. 9-8. Diagram Illustrating the Principle of the Mass Spectrometer

of a stiff spring. Let the bullets be ping-pong balls, and let us shoot them with a certain velocity at a target, which they strike again and again, at point A, in line with the barrel of the gun, as shown in the figure. Now we will suppose a steady wind to blow across the region between the gun and the target, and again shoot the balls. Since the ping-pong balls are very light in weight, they will be blown far off their original course and will strike the target, say, at B, and will do so again and again, at the same spot.

Let us now shoot a *heavier* ball, but one of the *same size* as before, so that the force of the wind acting upon it will be just the same as before. We could drill a small hole in a ping-pong ball, fill the inside with water to make the ball heavier, and seal the hole. We will then properly stretch the spring on the plunger to shoot this water-filled ball at the target with the same velocity as that possessed by the original ping-pong balls. This heavier ball, of greater mass and of more *inertia*, will not deviate (C) nearly as much as the lighter ball, though the force of the wind blowing on it is the same. Inertia is a fundamental property of all masses of matter (Fig. 2-1, p. 10). A heavy body is moved along or pushed aside much less than a lighter body, when the same force is acting.

The spots where the balls strike the target could be conveniently registered by making the target out of a soft, impressionable wax, or of white paper and covering the balls with lampblack. If we know the relative distances of the spots B and C from the spot A (undeviated balls), we can easily calculate the *relative weights* of the two balls *without having to weigh the balls*. The smaller the deviation, the heavier the ball.

The mass spectrometer works on the same principle. Instead of the ping-pong balls we have atoms carrying positive electric charges; instead

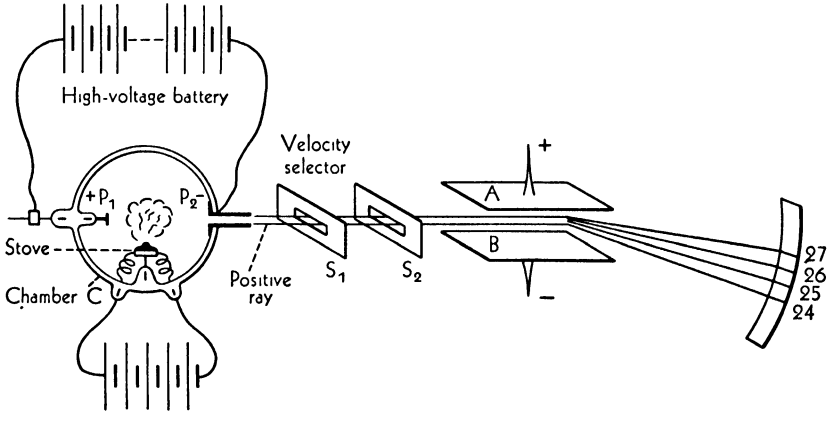


Fig. 9-9. Showing a Simplified and Idealized Mass Spectrometer

of the gun we have an accelerating chamber, which shoots the charged atoms out by electric means; instead of the wind we have an electric field to pull the particles from a straight-line path; instead of the wax target we have a photographic plate. The charged atoms, however, unlike the balls, do not all travel with the same speed until after they have passed through a velocity selector.

The Mass Spectrometer · The charged atoms are formed and accelerated in the chamber, C (Fig. 9-9). The system is evacuated, and P_1 and P_2 are connected to a high-voltage source so that P_1 is positive and P_2 negative. Under these conditions electrons leave P_2 and pass across the evacuated space to P_1. A very small amount of the element under investigation is introduced into the chamber as a gas or vapor. If it is not very volatile, it may be placed on a little electric stove, as shown, and some of it vaporized. As the atoms get into the path of the electrons moving from P_2 to P_1, some of their own electrons are knocked off, which leaves them positively charged. These positively charged atoms are attracted to the negative electrode, P_2, and move rapidly toward it. By the time they reach it, they are traveling at a very high speed. Most of them collide with P_2 and stop, but some pass through a slit in P_2 and through a slit system S_1S_2, which acts as a velocity selector.

The beam of positive ions, all traveling at the same velocity, then passes into an electrostatic field between the two plates, A and B, which are charged electrically, and is bent downward toward the negative plate, B, being attracted by B and repelled by A. The light atoms are deflected more than the heavy ones (as the light ping-pong balls were deflected more than the heavy balls). Thus the atoms of different masses will be deflected as different beams, and will register on the photographic film in different lines, as shown in the figure; and from the extent of deviation from the original path the relative masses of the atoms can be calculated.

Actually, a mass spectrometer employs a magnetic rather than an electrostatic field. Or, if no velocity selector is used, the flying atoms (positively charged) pass first through an electrostatic and then a magnetic field. Regardless of their velocities, atoms of a given charge and mass can then be brought to a focus at a particular point.

Isotopes · When the elements were examined with the mass spectrometer, it was found that not all atoms of a given element have the same weight. For example, in the experiment which is illustrated in Fig. 9-9 magnesium was being examined, and the beam contained magnesium ions of masses 24, 25, 26, 27. The element chlorine has two different

kinds of atoms, of masses 35 and 37; nitrogen has atoms of masses 14 and 15; tin has ten different kinds of atoms. These different kinds of atoms are called *isotopes*; *they are atoms of the same element having different masses.* The isotopes of all the elements have masses either exactly equal to whole numbers or so nearly so that they are commonly regarded as having such masses (see Table of Isotopes in the Appendix).

The Percentage of Isotopes of an Element · Because the individual isotopes of a given element are not present in equal amounts, the *intensities* of the lines on a mass spectrogram are not the same. By measuring the intensities of these lines, it is possible to make a very accurate estimate of the *relative numbers* of the different isotopes which go to make up an element. For example, the relative abundance of the isotopes of chlorine is, for 35, 77.15 per cent; for 37, 22.85 per cent. The average weight of the mixture is, then,

$$(35 \times 0.7715) + (37 \times 0.2285) = 35.457.$$

This agrees with the atomic weight of chlorine determined by chemical methods. (Atomic weights can be determined, in general, considerably more accurately with the mass spectrometer than by chemical methods.)

Thus, it is evident that in nature the isotopes of an element are already mixed together and that the atomic weight is simply the average weight of a mixture of isotopes. This is the reason why atomic weights are often fractional values, whereas the isotope weights are whole numbers.

How Can an Element Have Atoms of Different Masses? The answer to this question has already been suggested in connection with the isotopes of hydrogen. In the nucleus of an atom there are protons and neutrons. The number of protons determines the number of positive charges on the nucleus and indirectly the chemical properties of the atom; the neutron has no charge, but has essentially the same mass as the proton, approximately 1 on the basis of O = 16. The protons and neutrons together give the mass of the nucleus. In some cases extra neutrons can be added to a nucleus, thus increasing the mass, without changing the positive charge on the nucleus, and hence without changing the chemical nature of the atom.

All atoms of magnesium contain 12 protons in their nuclei; but for the four isotopes the numbers of neutrons are 12, 13, 14, 15, thus giving the masses 24, 25, 26, 27, respectively. In the isotope 35 of chlorine there are 17 protons (17 +) and 18 neutrons, for a total mass of 35; whereas in isotope 37 there are 17 protons (17 +) and 20 neutrons, for a total mass of 37.

Prout's Hypothesis · Soon after the atomic theory was advanced (Dalton, 1805), the English physician Prout suggested that *all elements are really multiples*

of hydrogen, and that accurate determinations of atomic weights would show that they are whole numbers, based on hydrogen as unity. This hypothesis stimulated a great deal of splendid work; but the results all went to show that many weights are fractional, and the hypothesis was abandoned. Prout died in 1850, about eighty years too soon to see his prediction come true, although in quite a different manner from what he expected. For we have now learned that the elements of "fractional" atomic weights are really mixtures of atoms possessing whole-number weights, and that all the atoms (at least, their nuclei) are made up of protons, which are the nuclei of hydrogen atoms, and neutrons, which have the same mass as hydrogen atoms.

QUESTIONS

1. State the following laws and discuss their significance: (*a*) law of conservation of mass; (*b*) law of definite composition; (*c*) law of combining weights; (*d*) law of multiple proportions; (*e*) law of combining volumes.

2. In terms of the atomic theory account for (*a*) the law of definite composition; (*b*) the law of combining weights; (*c*) the law of multiple proportions; (*d*) the law of combining volumes. Give illustrations.

3. Distinguish between (*a*) atomic weight and gram-atomic weight; (*b*) weight of one atom and atomic weight; (*c*) "parts by weight" and percentage composition; (*d*) combining weight and atomic weight; (*e*) analysis and synthesis.

4. Outline the arguments that indicate that oxygen and hydrogen molecules are diatomic.

5. In 1811 chemists spoke of "Avogadro's hypothesis," but today they speak of "Avogadro's law." How can this change in terms be justified?

6. (*a*) What factors led to the choice of the oxygen atom as the standard for atomic weights? (*b*) Why was it assigned the value of 16 instead of 1 or 8?

7. (*a*) What weight of oxygen will contain the same number of oxygen atoms as the number of hydrogen atoms in 1.008 g of hydrogen? (*b*) What weight of carbon dioxide will contain this same number of molecules of carbon dioxide? Explain the reason for your answer in each case.

8. Explain logically, omitting no detail in the reasoning, how the molecular weight of a gas, referred to $O_2 = 32.000$, may be obtained by weighing a known volume of the gas of which the temperature and pressure have been determined.

9. Indicate what experimental data are necessary in order to determine the following: (*a*) molecular weight of a covalent compound; (*b*) specific heat of a solid element; (*c*) combining weight of an element; (*d*) percentage composition of a compound; (*e*) gram-molecular volume of a gas; (*f*) exact atomic weight.

10. Describe in detail the mass-spectrometer method for determining the masses of the isotopic atoms of an element and the atomic weight of the element.

11. (*a*) How can an element have atoms of different masses? (*b*) Why do such atoms of different masses have the same chemical properties?

12. (*a*) Knowing the molecular weight of a gaseous compound, how can you calculate the approximate weight of 1 liter of the gas? (*b*) How do you determine experimentally the exact weight of 1 liter of such a gas?

13. Outline the steps in the argument by which atomic weights are derived from combining weights, molecular weights, and percentage composition.

PROBLEMS

1. In an analysis of a compound of copper 1.42 g of the compound yielded 0.21 g of copper. What per cent of copper did the compound contain?

2. In determining the per cent of silver in a silver ore it was found that 2.12 g of the ore yielded 0.16 g of silver chloride (AgCl). Calculate the per cent of silver in the ore.

3. Copper forms two oxides. If 1 g of each of these oxides is reduced, separately, by the process described on page 94, 0.7989 g of copper is obtained from one of the oxides and 0.8882 g of copper from the other. From these data (*a*) calculate the combining weights of copper in the two cases, and (*b*) show that these combining weights are in accord with the law of multiple proportions.

4. One gram of a certain metallic element reacts with hydrochloric acid to liberate 1.245 liters of hydrogen at standard temperature and pressure. (*a*) What is the equivalent weight of the metal? (*b*) Its specific heat is 0.216. What is the approximate atomic weight of the metal? (*c*) What is the exact atomic weight? (*d*) What is the metal?

5. One liter of acetylene gas, measured under standard conditions, weighs 1.1621 g. What is the approximate molecular weight of the gas?

6. It was found that 1140 ml of a gas at 42° and 705 mm pressure weighed 0.6523 g. What was the molecular weight of the gas?

7. The molecular weight of hydrogen sulfide is 34.08. (*a*) Calculate the weight of 10 liters of hydrogen sulfide under standard conditions. (*b*) What is the weight of 10 liters of this gas at 25° and 730 mm pressure?

8. What is the weight of (*a*) 5 liters of sulphur dioxide; (*b*) 10 liters of carbon dioxide?

9. (*a*) A weight of 0.46 g of ethyl alcohol when vaporized at 100° occupies a volume of 302 ml at 760 mm pressure. Calculate the molecular weight of the alcohol. (*b*) If 11.1 g of ethyl alcohol is added to 500 g of water, the freezing point of the solution is found to be $-0.93°$. Calculate the molecular weight of the alcohol. (*c*) Compare the molecular weights obtained in (*a*) and (*b*) with the molecular weight calculated from the formula of ethyl alcohol, C_2H_6O.

10. The freezing-point constant for benzene is 5.1°. Calculate the molecular weight of a covalent compound of which 2.4 g, when dissolved in 160 g of benzene, lowers the freezing point of benzene to 3.1°. The freezing point of benzene is 5.5°.

11. Calcium combines with chlorine in the ratio 2.50 g of calcium to 4.43 g of chlorine. What is the combining weight of calcium?

12. (*a*) From the percentage of carbon present in each of the gases listed in the table below, and the weight of 1 liter of each (see the table in the Appendix, p. 818) calculate the approximate molecular weight of each and the part of the molecular weight due to carbon, and insert the values in the appropriate places

GASEOUS COMPOUNDS	PERCENTAGE OF CARBON BY EXPERIMENT	APPROXIMATE MOLECULAR WEIGHT DEDUCED FROM WEIGHT OF 1 LITER	PART OF MOLECULAR WEIGHT DUE TO CARBON
Carbon monoxide .	42.85		
Carbon dioxide . .	27.27		
Methane	74.85		
Acetylene	92.25		
Propane	81.70		

in the table. (*b*) Assuming that the molecules of at least one of the gaseous compounds given above contain but 1 atom of carbon, calculate the approximate atomic weight of carbon. (*c*) If the combining weight of carbon is 6.005, what must be the exact atomic weight of carbon?

13. The atomic weight of lithium is 6.840; it has two isotopes, of masses 6 and 7. Calculate the relative amounts of the two isotopes of lithium.

14. Calculate the atomic weight of neon, given that the relative amounts of the three isotopes of neon are, for mass 20, 90.4 per cent; for mass 21, 0.6 per cent; for mass 22, 9.0 per cent.

CHAPTER 10

FORMULAS; VALENCE; EQUATIONS; CHEMICAL CALCULATIONS

In Chapter 3 we indicated that symbols, formulas, and equations are used as chemists' shorthand to represent elements and compounds, and the reactions which elements and compounds undergo; and we have made use of symbols, formulas, and chemical equations in many of the preceding chapters. No discussion has yet been given, however, of the manner in which formulas are determined or of the rules governing the writing of equations. How do we know, for example, that the formula of potassium chlorate is $KClO_3$ and not K_2ClO_7 or some other combination of symbols and numbers? Why do we write

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

instead of

$$KClO_3 \longrightarrow KCl + O_2$$

as the equation for the decomposition of potassium chlorate?

Formulas of Compounds

Methods of Indicating the Composition of Compounds · When the composition of a compound has been determined by chemical analysis or synthesis, the results might be expressed for future use in several ways. One method would be to record the results of the experiment itself; for example, if we find that 0.0361 g of carbon combines with 0.0960 g of oxygen to form carbon dioxide, we can record that result by writing the proportions by weight of carbon and oxygen in carbon dioxide. However, it is more common practice to express the composition of compounds in terms of per cents, that is, in terms of the number of parts of each constituent in 100 parts of the compound. The percentages of the two elements in carbon dioxide are 27.3 per cent carbon and 72.7 per cent oxygen.

We know, however, that chemical combination occurs between certain numbers of *atoms* of two or more elements: it is therefore more useful to express the composition of a compound as a ratio of atoms rather than as a ratio by weight or percentage The composition expressed in terms of the ratio of atoms in the compound is indicated by the formula of the compound.

Calculation of the Ratio of Atoms in a Compound · The experimental data give us the ratio of elements by weight. To calculate the formula we must determine the ratio of elements by atoms. This is easily accomplished if we know the atomic weights of the elements, since by dividing the relative weight of each element by its atomic weight, we obtain at once the ratio of atoms.

Example. It is found experimentally (p. 129) that 0.0361 g of carbon combines with 0.0960 g of oxygen to form the compound carbon dioxide. What is the ratio of carbon atoms to oxygen atoms in carbon dioxide?

The ratio by weight is 0.0361 part of carbon to 0.0960 part of oxygen. The ratio by atoms will, then, be $\frac{0.0361}{12}$ atom of carbon to $\frac{0.0960}{16}$ atom of oxygen, where 12 and 16 are the atomic weights of carbon and oxygen respectively. The results of the division are $\frac{0.0361}{12} = 0.003$ and $\frac{0.0960}{16} = 0.006$. The atoms in the compound must be in a whole-number ratio, which may be found by dividing both numbers by the smaller; $\frac{0.003}{0.003} = 1$ atom of carbon combines with $\frac{0.006}{0.003} = 2$ atoms of oxygen. The ratio of atoms in carbon dioxide is thus 1 C : 2 O.

The Molecular Formula · The calculation of the ratio of atoms in the example just given does not necessarily give the formula of a molecule of carbon dioxide, since the ratio of one atom of carbon to two of oxygen is satisfied by the formula CO_2, C_2O_4, C_3O_6, or some higher multiple of CO_2. The choice between these must be made on the basis of the *molecular weight.* The molecular weights corresponding to the formulas just written would be

For CO_2	*For* C_2O_4	*For* C_3O_6
$C = 1 \times 12 = 12$	$2\ C = 2 \times 12 = 24$	$3\ C = 3 \times 12 = 36$
$2\ O = 2 \times 16 = \underline{32}$	$4\ O = 4 \times 16 = \underline{64}$	$6\ O = 6 \times 16 = \underline{96}$
Mol. wt = 44	Mol. wt = 88	Mol. wt = 132

We now compare the values of the molecular weight calculated as above from suggested formulas having the proper ratio of atoms, with the value of the molecular weight determined by experiment. Experimentally the molecular weight of carbon dioxide is found to be 44 (by obtaining the weight of 22.4 liters under standard conditions); hence the formula agreeing with this molecular weight is chosen, CO_2. A formula arrived at in this way is called the *molecular formula*, since it truly represents the formula for a molecule of the compound.

Formulas of Electrovalent Compounds; the Formula Weight · We learned in Chapter 4 that there are some compounds, the electrovalent compounds, which do not form true molecules, but only ordered piles of ions, whose total positive and negative charges are equal. For such a compound, therefore, we cannot determine a molecular weight, and we agree to use, as the formula, the simplest ratio of atoms or ions in the

compound. This formula is called the *simplest formula.* Similarly the weight obtained by adding the weights of the atoms in the formula is called the *formula weight,* and plays the same role in calculations as the molecular weight does for covalent molecules.

Example. The compound sodium chloride is found by experiment to contain 39 per cent sodium and 61 per cent chlorine. What is the simplest formula of sodium chloride?

The ratio by weight is 39 parts of sodium to 61 parts of chlorine. Dividing by the atomic weights, we find the ratio of atoms to be $\frac{39}{23}$ atoms of sodium to $\frac{61}{35.5}$ atoms of chlorine, or 1.7 : 1.7, or 1 : 1. The formula weight of sodium chloride is 22.997 plus 35.457, or 58.454.

Further examples of the calculation of formulas. 1. The compound methyl formate is found by experiment to contain 40.00 per cent carbon, 6.67 per cent hydrogen, and 53.33 per cent oxygen. At 120° and a pressure of 740 mm a 1-liter flask was found to contain 1.84 g of the gaseous compound. Calculate the formula of methyl formate.

The ratio of weights in the compound is 40.00 parts of carbon to 6.67 parts of hydrogen to 53.33 parts of oxygen. Dividing by the atomic weights, we find the ratio of atoms to be $\frac{40.00}{12} = 3.33$ atoms of carbon to $\frac{6.67}{1} = 6.67$ atoms of hydrogen to $\frac{53.33}{16} = 3.33$ atoms of oxygen. Dividing these in turn by the smallest number to get whole-number ratios, we have $\frac{3.33}{3.33} = 1$ atom of carbon to $\frac{6.67}{3.33} = 2$ atoms of hydrogen to $\frac{3.33}{3.33} = 1$ atom of oxygen. The formula of methyl formate is thus CH_2O, $C_2H_4O_2$, or some higher multiple of the simplest formula.

The choice between these is made by using the data in the problem to determine the molecular weight, by calculating the weight of 22.4 liters of gas under standard conditions. Converting the volume to standard conditions, we get

$$V = \frac{740 \times 1000 \times 273}{(120 + 273) \times 760} = 676 \text{ ml.}$$

This volume weighs 1.84 g; hence 22.4 liters will weigh $1.84 \times \frac{22400}{676} = 61$ g, and the molecular weight of methyl formate is 61. Summing the atomic weights,

$$\begin{aligned} 1\ C &= 1 \times 12 = 12 \\ 2\ H &= 2 \times\ 1 = \ 2 \\ 1\ O &= 1 \times 16 = \underline{16} \\ & \qquad\quad 30 \end{aligned}$$

shows that the molecular formula of methyl formate is not CH_2O but $C_2H_4O_2$, since the latter is the one which agrees with the experimentally determined molecular weight.

2. To determine the formula of silver oxide, an experimenter heated 1.8552 g of the compound until the oxygen was completely driven off; a silver residue weighing 1.7271 g remained (p. 128). Thus, the ratio of weights in the compound is 1.7271 g of silver combined with 0.1281 g of oxygen (1.8552 − 1.7271). The ratio of atoms is $\frac{1.7271}{107.9} = 0.016$ atom of silver to $\frac{0.1281}{16} = 0.008$ atom of oxygen. The whole-number ratio is $\frac{0.016}{0.008} = 2$ atoms of silver to $\frac{0.008}{0.008} = 1$ atom of oxygen,

or Ag_2O. Since we have no experimental molecular weight for silver oxide, we use the simplest formula.

Facts Expressed by Formulas · All the chemical compounds whose formulas are known had their formulas determined at some time by the methods just described. A formula, then, records the following experimental facts about a compound:

1. **The particular elements present in the compound.** All the elements whose symbols appear in the formula are present in the compound.

2. **The relative number of atoms of the elements.** The symbol itself represents *one* atom of the element; any number of atoms above one is indicated by a subscript number.

3. **The molecular or formula weight.** Since the formula specifies the number of each kind of atom, the weight corresponding to the formula is given by the sum of the weights of the atoms. This has been frequently illustrated in the sums given in the preceding paragraphs.

4. **The composition of the compound.** The formula makes it possible to calculate the proportions by weight of the different elements in the compound. In propane, C_3H_8, for example, there are 3×12 parts of carbon combined with 8×1 parts of hydrogen, in a total of 44 parts; or $\frac{36}{44}$ of propane is carbon and $\frac{8}{44}$ is hydrogen. If it is desired to express these proportions in percentages, we need only note that they may be calculated on the basis of 100 for the total weight of the compound.

Example. In one molecular weight of propane (C_3H_8) there are 44 parts: 36 parts of carbon and 8 parts of hydrogen:

$$\begin{aligned} 3\ C &= 3 \times 12 = 36 \\ 8\ H &= 8 \times\ 1 = \underline{\ 8} \\ & \qquad\quad 44 \end{aligned}$$

In 100 parts of propane there will be $\frac{36}{44} \times 100 = 81.8$ parts of carbon and $\frac{8}{44} \times 100 = 18.2$ parts of hydrogen, or propane contains 81.8 per cent carbon and 18.2 per cent hydrogen.

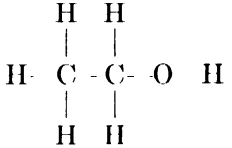
5. **The weight of a volume of gas.** If the formula, and hence the molecular weight, are known, we may also calculate *the weight of a given volume of a gaseous substance.*

Example. Calculate the weight of 5.6 liters of propane measured under standard conditions.

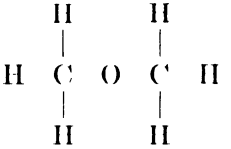
A volume of 22.4 liters of any gas under standard conditions will contain 1 g-mol. wt; 1 g-mol. wt of propane is 44 g. The weight of 5.6 liters is then obtained from the proportion

$$\frac{22.4}{5.6} = \frac{44}{x}, \quad \text{or} \quad x = 11 \text{ g of propane.}$$

Structural Formulas · A formula gives only the kind and number of atoms in a molecule; it does not show how the atoms are connected together. In order to show how the atoms are joined together we may draw *structural formulas*, using dash lines between the joined atoms (Chap. 4). Structural formulas are particularly useful in considering the compounds of carbon, for in compounds of carbon the same number and kind of atoms may be connected differently to give two or more different compounds. There are two compounds having the formula C_2H_6O, differing in their structural formulas.



ethyl alcohol



methyl ether

Valence

Early Concept of Valence · During the time that chemists were trying to solve the problem of whether the combining weights, or multiples of the combining weights, were the true atomic weights of the elements, the concept of *valence* was defined. As explained in Chapter 9, chemists did not know, at one time, whether the formula for water was H O or H O H. It was eventually proved convincingly, with Gay-Lussac's law of combining volumes and Avogadro's law (p. 80), that an atom of oxygen combines with *two* atoms of hydrogen. The atoms of other elements may differ from oxygen in the number of hydrogen atoms with which they combine.

Example 1.

HCl	H_2O	NH_3	CH_4
hydrogen chloride	water	ammonia	methane

The number of hydrogen atoms with which the atom of an element will combine is its valence. The valences of the atoms of these four elements, Cl, O, N, C, are respectively 1, 2, 3, 4. The hydrogen atom itself does not combine with more than one atom of any other element to form a compound that contains only two kinds of atoms; so it may be taken as the standard of valence. It has a valence of 1, and is called *univalent*. Atoms, like oxygen, of valence 2, are *bivalent*; like nitrogen, of valence 3, are *trivalent*; like carbon, of valence 4, are *tetravalent*. As a further example, several chlorine compounds may be considered.

Example 2.

NaCl	$ZnCl_2$	$AlCl_3$
sodium chloride	zinc chloride	aluminum chloride

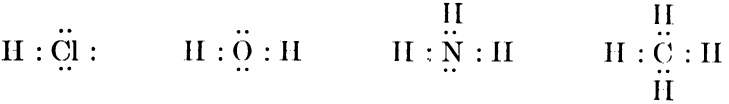
Here the atoms Na, Zn, Al, are combined with chlorine atoms, which also are *univalent*, like hydrogen, since 1 atom of chlorine combines with 1 atom of hy-

drogen in HCl; and the atoms Na, Zn, Al, will respectively displace 1, 2, 3 atoms of hydrogen from an acid. Their valences are, respectively, 1, 2, 3.

Valence was therefore defined by the early chemists as *the number of hydrogen atoms or other univalent atoms which an atom can hold in chemical combination or displace in a chemical reaction.*

Such a definition was very satisfactory. But when chemists came to recognize that there are two quite different kinds of compounds, those made up of atoms and those made up of ions, and when the new knowledge about atomic structure had shed more light on the nature of the chemical bonds between atoms and between ions, two new and more descriptive terms were adopted: *covalence* and *electrovalence.*

Covalence and Electrovalence · The *covalence* of an atom is defined, very much as valence is defined, as *the number of hydrogen atoms or other univalent atoms that the atom can hold in combination,* and as *the number of pairs of electrons shared with other atoms.* In the covalent compounds of Example 1 above, the covalence of the atoms is 1 for Cl, 2 for O, 3 for N, and 4 for C:



The *electrovalence* of an ion is *the number of univalent ions, like* H^+ *or* Cl^-*, which the ion can hold in chemical combination or displace in a chemical reaction; and it is the number of charges on the ion.* It is called *positive* electrovalence if the charge is positive, as in Na^+; and *negative* electrovalence if the charge is negative, as in Cl^-. In the electrovalent compounds of Example 2 above, the positive electrovalences of the ions Na^+, Zn^{++}, and Al^{+++} are $+1$, $+2$, and $+3$.

These two types of compounds can usually be distinguished by experimental test. Covalent compounds, when melted or when dissolved, usually in water, will not conduct an electric current appreciably. Electrovalent compounds, when so tested, will conduct an electric current strongly (by movement of the ions). There are some exceptions. Some compounds are intermediate in nature, partly covalent and partly electrovalent. Hydrogen chloride is covalent as a gas, but forms ions when it dissolves in water (hydrochloric acid). X-ray analysis will reveal whether or not a compound is composed of ions.

Electrovalence and Determination of a Formula · Electrovalent compounds are usually composed of metallic ions, which are positively charged, and nonmetallic ions, which are negatively charged. Some of the common ions are given in the table on the next page.

ELECTROVALENCES

NAME	IONS	ELECTRO-VALENCES	NAME	IONS	ELECTRO-VALENCES
Hydrogen	H^+	+1	Chloride	Cl^-	−1
Sodium	Na^+	+1	Bromide	Br^-	−1
Potassium	K^+	+1	Iodide	I^-	−1
Silver	Ag^+	+1	Oxygen	O^{--}	−2
Calcium	Ca^{++}	+2	Sulfide	S^{--}	−2
Magnesium	Mg^{++}	+2	Hydroxyl	OH^-	−1
Aluminum	Al^{+++}	+3	Nitrate	NO_3^-	−1
Ammonium	NH_4^+	+1	Sulfate	SO_4^{--}	−2
			Carbonate	CO_3^{--}	−2
			Phosphate	PO_4^{---}	−3

We must remember that these single charges of opposite sign, + or −, are always of the same size; one just balances, or neutralizes, the other. Any electrovalent compound is neutral; so the total number of + charges just balances the total number of − charges. The formula will show the same number of + charges as of − charges. The formula for sodium chloride is (Na^+, Cl^-) or NaCl; for calcium chloride it is (Ca^{++}, 2 Cl^-) or $CaCl_2$; for lime it is (Ca^{++}, O^{--}) or CaO; for aluminum chloride it is (Al^{+++}, 3 Cl^-) or $AlCl_3$; for iron sulfide it is (Fe^{++}, S^{--}) or FeS; and for sodium oxide it is (2 Na^+, O^{--}) or Na_2O.

Example. What is the formula of aluminum oxide?

Since the electrovalence of aluminum is +3 and that of oxygen is −2, the charges can balance only if we take two aluminum ions and three oxygen ions: $2 \times (+3) + 3 \times (-2) = 0$. Hence the formula is Al_2O_3. The formula Al_4O_6 is also possible; but unless other information requires it, the simplest formula is chosen.

Radical Ions, or Complex Ions · In many chemical reactions there are groups of atoms the members of which remain attached to one another. When sulfuric acid reacts with zinc, the group SO_4 does not separate into individual atoms:

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

These groups are called *radicals*, and many, like SO_4, occur as ions; thus, SO_4^{--} is the sulfate ion. There are both positive and negative radical ions, or complex ions, such as NH_4^+, SbO^+, CO_3^{--}, NO_3^-, OH^-, PO_4^{---}. In the determination of formulas these radical ions may be treated as units, just like single ions, and taken in proper number to balance the oppositely charged ions.

Variable Valence · It often happens that two given elements form more than one compound, and, in such cases, at least one of the elements

must have more than one valence. Iron unites with chlorine to form two compounds, ferrous chloride ($FeCl_2$) and ferric chloride ($FeCl_3$), in which iron has positive electrovalences of 2 and 3 respectively. Other metallic ions have different electrovalences under different conditions of chemical reaction. It is this variable valence that gives more than one combining weight to elements. The particular one of its variable valences which an element adopts in a chemical reaction depends upon the substances with which it is reacting and, sometimes, the conditions of the reaction. For example, when iron reacts with hydrochloric acid, it forms $FeCl_2$; but when it reacts with free chlorine, it forms $FeCl_3$.

Oxidation Number, or Oxidation State · The concept of valence, as defined thus far, is applicable to, and adequate for, the case of simple ions and most compounds which are composed of only two different kinds of atoms (called binary compounds). But there are many compounds for example, those made of three different elements (called ternary compounds), and especially compounds containing complex ions, or radical ions, like SO_4^{--} in H_2SO_4, NO_3^- in HNO_3, ClO_3^- in $KClO_3$, etc. in which the distinction between electrovalence and covalence cannot always be easily and clearly made. The treatment of such cases can better be made in terms of *oxidation number*, or *oxidation state*; and this treatment will be explained when we discuss oxidation-reduction reactions in Chapter 15.

Equations

What Is a Chemical Equation? A chemical equation is simply a sentence written with chemical symbols and formulas; it represents with symbols and formulas the rearrangement of atoms and molecules during a reaction; it is a record, in chemical notation, of what molecules and how many molecules enter into the reaction and what molecules and how many molecules are formed. For example:

In words: Two molecules of hydrogen react with one molecule of oxygen to form two molecules of water.

In equation form: $2\,H_2 + O_2 \longrightarrow 2\,H_2O$

It must be emphasized that an equation merely represents *facts which are already known from experiment.* In other words, we cannot attempt by equation-writing to find out what the products of a chemical reaction are, or what their formulas are; but having found by experiment what chemical change takes place, we can record the facts in an equation.

Steps in Writing an Equation · 1. The *first* step in writing an equation, therefore, is to *recall what substances react and what products are formed.*

It may be worth while to write down a qualitative statement—for example, "Potassium chlorate decomposes to give potassium chloride and oxygen." There must be no doubt about the correctness of such a statement; if there is any doubt, it is useless to toy with the remaining steps.

2. The *second* step consists in *writing down the formulas of the reactants and the products.* These formulas must agree, of course, with the known facts concerning the composition of the compounds. In many cases a knowledge of the valences of the elements involved will help in writing formulas correctly; other facts must simply be remembered—for example, that the formula of the oxygen molecule is O_2, and not O or O_4. For the potassium chlorate example above, then, we should have, after completing the second step,

$$KClO_3 \longrightarrow KCl + O_2$$

3. The *third* step consists in *balancing the equation*; this involves making the numbers of each kind of atom the same on the two sides of the equation. This is required by the law of conservation of mass, since there may be no gain or loss of atoms as a result of a reaction. The equation given in step 2 is not balanced. It is not balanced because, while there is one atom each of potassium and chlorine in both the reactant and the products, there are three atoms of oxygen in the reactant ($KClO_3$) and only two (O_2) in the products, as written above. In order to make the equation balance, it must be changed so that there is the same number of oxygen atoms in the reactant and the products. The simplest way to arrive at this result is to choose six atoms of oxygen; the balanced equation

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

is then obtained. Note that the formulas of the compounds involved in the reaction are definitely fixed; the equation is balanced only by finding the correct number of moles of each substance, in order to make the number of atoms of each element the same in the reactant and in the products. The completed equation then records the experimental facts that two moles of potassium chlorate (having the formula given) decompose to produce two moles of potassium chloride (formula, KCl) and three molecules of oxygen (diatomic).

Facility in balancing equations comes largely from practice. It is usually convenient, however, to work back and forth from one side of the arrow to the other, as shown in the following example:

Example. Reaction of hot carbon with steam.

Step 1. The chemical facts. Hot carbon reacts with steam to form hydrogen and carbon dioxide, which has the formula CO_2.

Step 2. Formulas of reactants and products.

$$C + H_2O \longrightarrow CO_2 + H_2$$

Step 3. Balancing. In the products, on the right-hand side, there are two atoms of oxygen. These must have come from the water; so two molecules of water are required:

$$C + 2\ H_2O \longrightarrow CO_2 + H_2$$

But two molecules of water contain four hydrogen atoms; these must appear in the products:

$$C + 2\ H_2O \longrightarrow CO_2 + 2\ H_2$$

The equation is now balanced, and it records the chemical facts that one atom of carbon reacts with two molecules of water to form one molecule of carbon dioxide and two molecules of hydrogen.

Generalized Statements of the Chemical Facts · While it is true that the experimental facts must be known before an equation can be written, it is not necessary to remember these facts for every two substances which a chemist could conceivably mix. Chemical compounds fall into certain general classes, and the members of a particular class show similar behaviors toward members of another class. It is thus possible to make generalized statements of the chemical facts relating to the reactions of classes of compounds or to the reactions between classes of compounds; these generalized statements can then be particularized to apply to a specific compound in a class, as need arises. Several of these generalized statements have been made in the preceding chapters; the student should watch for and memorize those which he meets in the future.

Example 1. Reaction of phosphoric oxide with water.

Phosphoric oxide belongs to the class of compounds known as oxides of nonmetals. A generalized statement about this class of compounds is that they react with water to form acids (p. 53). Consequently,

Step 1. Phosphoric oxide reacts with water to form an acid. Since it is phosphoric oxide, it must form a phosphoric acid.

Step 2. The formula of phosphoric oxide is P_4O_{10}; the common phosphoric acid has the formula H_3PO_4:

$$P_4O_{10} + H_2O \longrightarrow H_3PO_4$$

Step 3. The four atoms of phosphorus on the left must appear on the right; this requires four molecules of phosphoric acid:

$$P_4O_{10} + H_2O \longrightarrow 4\ H_3PO_4$$

The four molecules of phosphoric acid contain sixteen atoms of oxygen; ten of these are already accounted for in the molecule of phosphoric oxide, which leaves six more to be furnished by the water:

$$P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4$$

The six molecules of water contain twelve atoms of hydrogen; these are just sufficient to make twelve available for the four molecules of phosphoric acid, and the equation is balanced. It records the chemical facts that when one molecule of phosphoric oxide reacts with six molecules of water, four molecules of phosphoric acid of the formula H_3PO_4 are formed.

Example 2. Decomposition of mercuric oxide by heating.

Mercuric oxide belongs to the class of compounds known as oxides of the noble metals. A generalized statement about this class of compounds is that they decompose on heating to yield oxygen and the metals. Consequently,

Step 1. Mercuric oxide decomposes on heating to form mercury and oxygen.

Step 2. The formula of mercuric oxide is HgO; oxygen is diatomic:

$$HgO \longrightarrow Hg + O_2$$

Step 3. The two oxygen atoms on the right must be present on the left; this requires two moles of mercuric oxide:

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

But two moles of mercuric oxide contain two gram-atoms of mercury; they must appear on the right:

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

The balanced equation records the chemical facts that two moles of mercuric oxide decompose to form two gram-atoms of mercury and one mole of oxygen.

Example 3. Reaction of zinc with dilute sulfuric acid.

Sulfuric acid is an acid; zinc is a metal, and it is above hydrogen in the electrochemical series. A generalized statement of the chemical facts relating to substances of this sort is that dilute sulfuric and all other common acids (except nitric acid) react with metals above hydrogen in the electrochemical series to produce hydrogen and a salt (p. 86). Consequently,

Step 1. Zinc reacts with sulfuric acid to produce hydrogen and a salt.

Step 2. The formulas of zinc, sulfuric acid, and hydrogen are known. The salt must be the one produced by displacing the hydrogen of the sulfuric acid with zinc; since the electrovalence of zinc is + 2 and of the sulfate radical is − 2, its formula is $ZnSO_4$:

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

Step 3. The equation is already balanced, as it stands, and states that one gram-atom of zinc reacts with one mole of sulfuric acid to form one mole of zinc sulfate and one mole of hydrogen.

Indicating the Conditions of Reaction · In general, an equation does not indicate the conditions under which a reaction takes place. For example, the equation

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

does not show that hydrogen chloride must be dissolved in water if the reaction is to take place. Sometimes additional conventions are adopted to give more information than that shown by the equation itself. One may write, for instance,

$$2\ KClO_3 \xrightarrow[MnO_2]{\Delta} 2\ KCl + 3\ O_2\uparrow$$

to show that potassium chlorate is heated (Δ) in the presence of the catalyst manganese dioxide, and that the oxygen is evolved as a gas ($\uparrow$). The formation of an insoluble precipitate may be indicated by $\downarrow$:

$$Ba(OH)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2\ H_2O$$

Another convention indicates the energy change in the reaction by showing the heat evolved or absorbed when *gram-formula weights* of the substances are used. Thus the equation

$$Fe + S \longrightarrow FeS + 24{,}000\ cal$$

states that when a gram-formula weight, 87.91 g, of iron sulfide is formed, 24,000 cal of heat is evolved.

Such a reaction in which heat is evolved is called an *exothermic reaction*; and one like the decomposition of mercuric oxide, where heat is absorbed, is called *endothermic*.

Chemical Calculations

Calculations from Equations · The equation expresses the relationships between the *numbers of molecules* reacting and the numbers of molecules formed in a chemical reaction. Knowing the molecular weights, the chemist can translate this into relationships between the *weights* of substances reacting and the weights of substances formed in the reaction. This is convenient because it enables him to calculate how much material he can prepare from a given weight of starting material or how much starting material is required to obtain a given weight of product.

1. ***Weight Relationships*** · **Example 1.** What weight of hydrogen can be prepared by the action of sulfuric acid on 98.1 g of zinc?

One needs first a correctly written and balanced equation; it is

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

What does the equation say? It says that one atom of zinc will produce one molecule of hydrogen, or that 1 g-at. wt (1 mole) of zinc will produce 1 g-mol. wt (1 mole) of hydrogen; hence

65.4 g of zinc will produce 2 g of hydrogen.

What does the problem ask? It asks how much hydrogen, x, will be produced by 98.1 g of zinc.

98.1 g of zinc will produce x g of hydrogen.

Solving the proportion $$\frac{65.4}{98.1} = \frac{2}{x},$$

we get $$x = \frac{98.1 \times 2}{65.4} = 3 \text{ g hydrogen.}$$

It is often helpful to write the gram-atomic weights and the gram-molecular weights, and the quantities involved in the problem, directly under the symbols and formulas of the equation, as follows:

$$\begin{array}{ccc} Zn + H_2SO_4 & \longrightarrow & ZnSO_4 + H_2 \\ \frac{65.4}{98.1} & = & \frac{2}{x}. \end{array}$$

$$x = 2 \times \frac{98.1}{65.4} = 3 \text{ g hydrogen.}$$

Example 2. How much sodium peroxide must be used in order to prepare 80 lb of oxygen?

One needs first a correctly written and balanced equation for the formation of oxygen from sodium peroxide; it is

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

What does the equation say? It says that two moles of sodium peroxide will produce one mole of oxygen, or that 2 pound-formula wt of sodium peroxide will produce 1 pound-formula wt of oxygen; hence

2×78 lb Na_2O_2 will produce 32 lb O_2.

$2\ Na = 2 \times 23 = 46$
$2\ O = 2 \times 16 = 32$
78

What does the problem ask? It asks how much sodium peroxide is needed to produce 80 lb of oxygen.

x lb Na_2O_2 will produce 80 lb O_2.

Solving the proportion $$\frac{2 \times 78}{x} = \frac{32}{80},$$

we get $$x = \frac{2 \times 78 \times 80}{32} = 390 \text{ lb } Na_2O_2.$$

This may be summarized in this manner:

The equation: $2\ Na_2O_2 + 2\ H_2O \longrightarrow 4\ NaOH + O_2$

The formula quantities: 2×78 32

The problem: x 80

The proportion: $$\frac{2 \times 78}{x} = \frac{32}{80}.$$

The solution: $$x = \frac{2 \times 78 \times 80}{32} = 390 \text{ lb.}$$

2. ***Weight-Volume Relationships*** · Remembering that a gram-molecular weight of a gas under standard conditions occupies 22.4 liters, we can calculate the volumes of gases produced by or required to react with a certain quantity of a compound.

Example. What volume of hydrogen, measured at 760 mm and 0°, would be necessary to reduce 25 g of copper oxide?

To solve the problem a correctly written and balanced equation is necessary; it is

$$H_2 + CuO \longrightarrow Cu + H_2O$$

The equation states that 1 mole of hydrogen is required for each mole of copper oxide; hence, under standard conditions, 22.4 liters of hydrogen is needed for 1 gram-formula wt of copper oxide, or

22.4 liters H_2 will reduce 79.6 g CuO.

Cu = 63.6
O = 16
79.6

We want to know the volume of hydrogen required to reduce 25 g of copper oxide:

x liters H_2 will reduce 25 g CuO.

Solving the proportion $$\frac{22.4}{x} = \frac{79.6}{25},$$

we get $$x = \frac{25 \times 22.4}{79.6} = 7.03 \text{ liters } H_2.$$

This may be summarized in this manner:

The equation: $H_2 + CuO \longrightarrow Cu + H_2O$

The formula quantities: 22.4 79.6

The problem: x 25

The proportion $$\frac{22.4}{x} = \frac{79.6}{25}.$$

The solution: $$x = \frac{22.4 \times 25}{79.6} = 7.03 \text{ liters.}$$

The validity of this result may be roughly checked by observing that 25 g of copper oxide is about $\frac{25}{80}$, or $\frac{5}{16}$ gram-formula wt, so that $\frac{5}{16}$ g-mol. wt of hydrogen will be required. Five sixteenths of a gram-molecular weight of hydrogen will occupy five sixteenths of a gram-molecular volume, or about 7 liters, which agrees with the calculated result.

3. ***Volume-Volume Relationships*** · When two or more of the substances used or formed in a chemical reaction are gases one may use gram-molecular volumes, or any fractions thereof, in calculating volumes of reactants or products, provided the volumes are measured at the same temperature and pressure. Thus, when

nitrogen and hydrogen react, ammonia, which is also a gas, is formed according to the equation

$$N_2 + 3\ H_2 \longrightarrow 2\ NH_3$$

The equation not only tells us that one mole of nitrogen reacts with three moles of hydrogen to form two moles of ammonia, but it also tells us that one volume of nitrogen reacts with three volumes of hydrogen to form two volumes of ammonia. This interesting relationship follows from Avogadro's law (pp. 80, 132), and is an expression of Gay-Lussac's law of combining volumes (p. 132).

Example. What volume of hydrogen gas is required to react with 40 liters of nitrogen gas, both volumes to be measured at the same temperature and pressure?

The equation: $N_2 + 3\ H_2 \longrightarrow 2\ NH_3$

The proportion for the problem is:

$$\frac{1}{40} = \frac{3}{x} \text{ where } x \text{ is the volume of hydrogen required.}$$

$x = 120$ liters of hydrogen used.

4. ***Sequence of Reactions*** · When a product is obtained as the result of a sequence of reactions, it is not necessary to calculate the weights of the product formed in the first reaction if this product is to be used again in the second. Instead the ratio of moles of reactants to moles of products may be obtained directly from the equations. This is illustrated in the next example.

Example. Aluminum chloride is to be prepared from aluminum sulfate by the reactions

(1) $Al_2(SO_4)_3 + 6\ NaOH \longrightarrow 2\ Al(OH)_3 + 3\ Na_2SO_4$
(2) $Al(OH)_3 + 3\ HCl \longrightarrow AlCl_3 + 3\ H_2O$

How much aluminum chloride can be obtained from 17.1 g of aluminum sulfate?

The equations say (1) that one mole of aluminum sulfate will produce two moles of aluminum hydroxide:

$$Al_2(SO_4)_3 \longrightarrow 2\ Al(OH)_3$$

and (2) that one mole of aluminum hydroxide will produce one mole of aluminum chloride:

$$Al(OH)_3 \longrightarrow AlCl_3$$

Hence one mole of aluminum sulfate will produce two moles of aluminum chloride:

$$Al_2(SO_4)_3 \longrightarrow 2\ Al(OH)_3 \longrightarrow 2\ AlCl_3$$

or

$$342\text{ g } Al_2(SO_4)_3 \text{ will produce } 2 \times 133.5\text{ g } AlCl_3.$$

The problem asks how much aluminum chloride can be made from 17.1 g of aluminum sulfate, and may be solved as follows:

$$\frac{342}{17.1} = \frac{2 \times 133.5}{x};$$

therefore

$$x = \frac{17.1 \times 2 \times 133.5}{342} = 13.35\text{ g } AlCl_3.$$

QUESTIONS

1. Define the terms (*a*) symbol; (*b*) formula; (*c*) equation; (*d*) covalence; (*e*) electrovalence; (*f*) simplest formula; (*g*) molecular formula; (*h*) covalent bond; (*i*) electrovalent compound; (*j*) covalent molecule.

2. What experimental data are necessary to determine (*a*) the simplest formula? (*b*) the molecular formula?

3. Interpret the symbols and formulas listed below, in the manner indicated by the column headings.

FORMULA	ELEMENTS PRESENT	NUMBER OF ATOMS OF EACH ELEMENT	FORMULA WEIGHT	PER CENT OF EACH ELEMENT IN THE COMPOUND
a. O_3				
b. CH_4				
c. Na_2O_2				
d. $KClO_3$				
e. P_4O_{10}				
f. $Al_2(SO_4)_3$				

4. From the following formulas determine the valences of the elements and radicals that are underlined. (The valence of hydrogen is + 1, and of oxygen − 2.) (*a*) $\underline{Fe}O$; (*b*) $\underline{Fe_2}O_3$; (*c*) $\underline{H}Cl$; (*d*) $\underline{Hg}Cl_2$; (*e*) $H_2\underline{CO_3}$; (*f*) $H_3\underline{PO_4}$; (*g*) $\underline{Ba}CO_3$; (*h*) $\underline{Ca_3}(PO_4)_2$.

5. From the valences given on page 155, determine the formula for the compound formed between the ions in each of the following pairs:

a. Na^+ and O^{--}
b. Ca^{++} and Cl^-
c. Al^{+++} and Cl^-
d. Al^{+++} and O^{--}
e. NH_4^+ and SO_4^{--}
f. K^+ and PO_4^{---}
g. Mg^{++} and PO_4^{---}
h. Ca^{++} and SO_4^{--}

6. Balance the following equations, in which the symbols and formulas for reactants and products are given:

a. $Fe_2O_2 + CO \longrightarrow Fe + CO_2$
b. $CH_4 + O_2 \longrightarrow CO_2 + H_2O$
c. $Al + HgCl_2 \longrightarrow AlCl_3 + Hg$
d. $Fe_3O_4 + H_2 \longrightarrow Fe + H_2O$

7. (*a*) List the steps necessary in writing and balancing chemical equations. (*b*) Give the reason for each step. (*c*) Complete and balance the following equations. (*d*) Indicate any special conditions required to make the reactions take place.

a. $HgO \longrightarrow$
b. $KClO_3 \longrightarrow$
c. $H_2O \longrightarrow$
d. $H_2O_2 \longrightarrow$
e. $C + H_2O \longrightarrow$
f. $Mg + H_2O \longrightarrow$
g. $CO_2 + Ca(OH)_2 \longrightarrow$
h. $CaCl_2 + H_2O \longrightarrow$
i. $P + O_2 \longrightarrow$
j. $Al + H_2SO_4 \longrightarrow$

8. What type of product should you expect to get (p. 158) from the following indicated reactions? Complete and balance the equations.

a. $CO_2 + H_2O \longrightarrow$
b. $Na_2O + H_2O \longrightarrow$
c. $Ag_2O \longrightarrow$
d. $Na + H_2O \longrightarrow$
e. $Fe + HCl \longrightarrow$
f. $H_2O_2 \longrightarrow$

PROBLEMS

1. Calculate the percentage composition of each of the following compounds from the number of grams of each element in the compound:

a. Hydrogen, 0.5 g
Oxygen, 4.0 g

b. Carbon, 3 g
Hydrogen, 1 g
Oxygen, 4 g

c. Carbon, 3 g
Oxygen, 8 g

2. From the formula calculate the percentage composition of each of the following compounds: (*a*) H_2O; (*b*) H_2O_2; (*c*) CO_2; (*d*) $CuSO_4 \cdot 5\,H_2O$.

3. *a.* From the formula calculate the formula weight of each of the following compounds: $KClO_3$; HCN; Na_2SO_4.

b. Calculate the percentage composition of the compounds in *a*.

c. Calculate the simplest formulas for the compounds whose compositions are given below, and compare the formulas with those given in *a*.

K = 31.97 per cent
Cl = 28.69 per cent
O = 39.34 per cent

H = 3.70 per cent
C = 44.44 per cent
N = 51.85 per cent

Na = 32.39 per cent
S = 22.53 per cent
O = 45.07 per cent

4. An oxide of lead has the composition 86.61 per cent lead and 13.39 per cent oxygen. What is the simplest formula of the oxide?

5. It is found that 15.5 g of phosphorus combines with 12 g of oxygen to form a compound whose molecular weight is 220. What is the molecular formula of the compound?

6. The gaseous compound ethane is composed of carbon and hydrogen in the ratio by weight of 4 to 1. One liter of ethane under standard conditions weighs 1.356 g. Calculate the molecular formula of ethane.

7. The common anesthetic chloroform is a colorless liquid boiling at 61°. Its molecular weight is approximately 119. Analysis shows that it contains carbon, hydrogen, and chlorine in the following proportions: carbon, 10.05 per cent; hydrogen, 0.84 per cent; chlorine, 89.10 per cent. Calculate its formula.

8. What weight of hydrogen can be prepared by the action of sulfuric acid on 60 g of magnesium?

9. Two and five-tenths grams of potassium chlorate was heated to drive off the oxygen, and the gas was collected over water at 23° and 742 mm pressure. What volume of gas was obtained?

10. A certain compound contains 7.7 per cent hydrogen and 92.3 per cent carbon. At 100° and 740 mm, 1.0 g of the gaseous compound is found to occupy 403 ml. What is the formula of the compound?

11. When 1.5 g of a gaseous compound of carbon and hydrogen was burned, there were formed 4.4 g of carbon dioxide and 2.7 g of water. The weight of 1 liter of this compound at standard conditions was 1.34 g. What is the molecular formula of the compound?

12. A certain compound contains 40 per cent carbon, 6.67 per cent hydrogen, and 53.33 per cent oxygen. A solution of 3 g of this compound, dissolved in 100 g of water, freezes at $-0.31°$. What is the formula of the compound?

13. Suppose you wish to prepare 1 kg of the ordinary medicinal hydrogen peroxide. What compounds will be required, and what weight of each?

14. Calculate the weight of oxygen required to combine with 100 liters of hydrogen (measured under standard conditions) to form water.

15. Five grams of zinc was added to sulfuric acid containing 10 g of hydrogen sulfate. Calculate the volume of hydrogen liberated.

16. How much sodium carbonate must be used to prepare 220 g of carbon dioxide by the action of hydrochloric acid on the sodium carbonate? The equation for the reaction is

$$Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + H_2O + CO_2$$

17. Native sulfur ore, containing some rock impurities, was used for the preparation of sulfuric acid. The reactions were

$$S + O_2 \longrightarrow SO_2$$
$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

From 10 g of the ore, 29.4 g of sulfuric acid was obtained. What was the percentage of sulfur in the ore?

18. A compound of carbon, hydrogen, and oxygen was burned completely in oxygen, and the resulting carbon dioxide and water vapor were collected. It was found that 0.69 g of the compound produced 1.32 g of carbon dioxide and 0.81 g of water. The freezing point of a solution containing 1.38 g of this compound in 20 g of water was $-2.79°$. What is the formula of the compound?

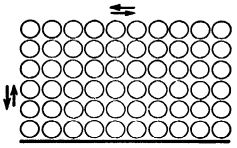
19. In a certain compound arsenic and oxygen are combined in the ratio 5.0 lb of arsenic to 1.6 lb of oxygen. A volume of 13.6 cu ft of this compound, measured at 140° F and at 15 lb/sq in., weighs 12 lb 8 oz. What is the molecular formula of the compound?

CHAPTER 11

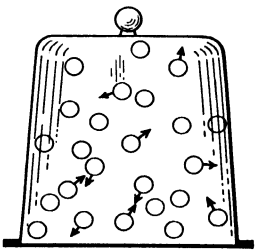
THE STATES OF MATTER AND THEIR TRANSITIONS; CRYSTAL STRUCTURE

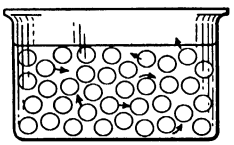
Kinetic Energy of Particles and Attractive Forces between Particles. In any crowd of particles of matter (that is, in any body of matter) we can recognize two opposing tendencies. (1) There is the tendency of the particles to fly apart because of their kinetic energy, and (2) there is the tendency of the particles to be drawn together by attractive forces.

1. The kinetic energy of the molecules, $\frac{1}{2}mv^2$, previously discussed in connection with the kinetic-molecular theory in Chapter 6, is proportional to the absolute temperature. If the temperature is raised higher and higher, the kinetic energy becomes greater and greater, and particles that may have been existing in the liquid state may then overcome completely the attractive forces holding them together, break away from one another, and fly apart, thus passing from the liquid into the gaseous state and expanding to fill any containing vessel.



Particles of a Solid, Close-packed and Fixed in an Ordered Pattern, but Vibrating Back and Forth, In and Out, Up and Down





Particles of a Liquid, Almost as Close-packed as Those of a Solid, but Gliding over One Another in a Random Manner

Particles of a Gas or Vapor, Relatively Far Apart, Moving Randomly, Colliding with One Another and with the Walls of the Vessel

Fig. 11-1

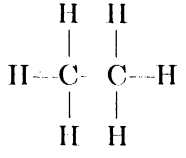
On the other hand, if we start with a gas and lower the temperature more and more, eventually the kinetic energy of the molecules will become so small that their attractive forces will be able to grip them and to bind them into a liquid, where they will be held closely in contact but free to glide over one another; and at a still lower temperature, to bind

them even more tightly into a solid crystal, where they cannot glide about, but only oscillate in fixed positions.

2. The molecular forces of attraction, often called *van der Waals forces,* are physical in their nature and are not to be confused with forces of chemical bonding. They do not bring about chemical combination, but they do lead to the condensation of gases to liquids (and solids) and are responsible for holding the particles of a liquid and of a solid together so that they are closely packed and form a coherent body. These forces are enormously greater than the force of gravity (of the order of a billion times greater), and they fall off rapidly with increasing distance between the molecules, and so are effective only when the molecules are fairly close together. The strength of the forces is different for different kinds of molecules. We have already mentioned, on page 73, that the attractive forces are stronger in water molecules than in hydrogen molecules, and that water vapor deviates more from the gas laws than does hydrogen. Water vapor can be readily liquefied at room temperature, but hydrogen gas must be cooled far below 0° and the kinetic energy greatly reduced, before it will condense to a liquid.

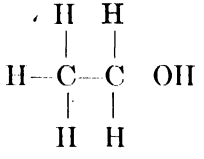
A similar increase in the forces of attraction, due to the presence of oxygen atoms, is noted in many compounds.

Examples of Varying Attractive Forces · 1. Suppose we have a sample of ethane. This substance is made up of molecules of the formula



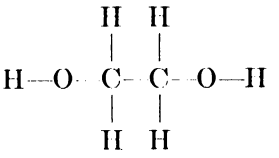
Here the attractive forces between molecules are small, and at room temperature ethane is a gas.

2. But if the ethane molecules are changed chemically, by the addition of an oxygen atom to every molecule,

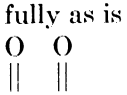


to give *ethyl alcohol,* the attractive forces between molecules become stronger. At room temperature these molecules of ethyl alcohol are held largely in the *liquid* state, but above 78° the molecules will occur largely in the gaseous state.

3. If we add a second oxygen atom to every molecule,



we get *ethylene glycol*, which at room temperature is a liquid, and the molecules are held together so strongly that the liquid is viscous (resistant to flow, like molasses); and the liquid is much less volatile (evaporates much less readily) than ethyl alcohol.

4. Finally, by loading the two carbon atoms of the original ethane molecule with oxygen atoms as fully as is chemically possible, we get the molecule of *oxalic acid*,  . Here the attractive forces are so extremely strong that the molecules are bound into a rigid, crystalline solid, practically nonvolatile at room temperature. In all four of these examples, a struggle between the tendency to fly apart and the tendency to be drawn together is, of course, going on. Here, working at constant temperature (room temperature), we have progressively favored the tendency of the molecules to be drawn together, in our stepwise addition of oxygen atoms, just as we can favor, for any given kind of molecule, the tendency to fly apart by raising the temperature higher and higher.

Transition between Liquids and Gases

Liquids and Gases · Liquids, as we might expect, differ from gases in that they do not distribute themselves uniformly throughout the whole volume of a containing vessel, but retain their own volumes. Because of their mobility, however, liquids do take the shape of the portion of the containing vessel which they occupy. Further, liquids contract only slightly even upon application of great pressure—a result which finds a ready interpretation in terms of our picture of the molecules of a liquid as being already crowded together with little free space between molecules. (See Fig. 6-3, p. 62.)

Evaporation · When a liquid such as water is placed in an open vessel, it gradually passes into the air in the form of gas or vapor, and the process is called *evaporation*. In a confined space, as in a closed bottle (Fig. 11-2), evaporation proceeds until the air above the liquid contains a definite

percentage of gaseous water, and then apparently ceases; the air is said to be *saturated* with water vapor. It is only *apparently* that the process ceases, as we can understand if we consider the question from a kinetic point of view. The molecules of a liquid are in random heat-motion, some of them at speeds greater than the average and others at speeds less than the average. From the surface of the liquid the more rapidly moving molecules will escape, breaking free from the attraction of their neighbor molecules. They will then move about in the air space above as gas molecules, and, as more and more of them accumulate there, many will strike the surface of the liquid and will return to the liquid, as represented in Fig. 11-2. Eventually enough molecules of water vapor will accumulate in the air space so that the number returning to the liquid in one second will be equal to the number escaping from the liquid into the vapor in the same time, and a state of balance, or equilibrium, will be reached. Although molecules continue to escape, there is no further *net* loss of molecules from the surface. The space above the liquid is *saturated* with the vapor, and the equilibrium between the tendencies to escape into the gas space (evaporation) and to return to the liquid (condensation) may be represented in the following manner:

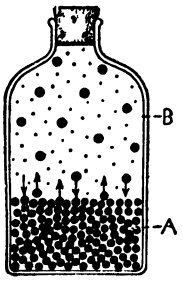


Fig. 11-2. Diagram of a Liquid (large black dots, A) Evaporating into Air (small dots, B) in a Closed Bottle

$$\text{Liquid} \rightleftarrows \text{vapor}$$

That it is the more rapidly moving molecules which escape during the evaporation of a liquid is evidenced by the fact that a liquid is cooled by the process of spontaneous evaporation, that is, by the escape of the more active ("hot") molecules.

Vapor Pressure · The pressure of the saturated vapor in equilibrium with the liquid is the *vapor pressure* of the liquid. It is commonly *expressed in millimeters of mercury*, and it is a measure of the volatility of the liquid, or the tendency of the liquid to evaporate. The vapor pressure is almost exactly the same, whether the saturated space above

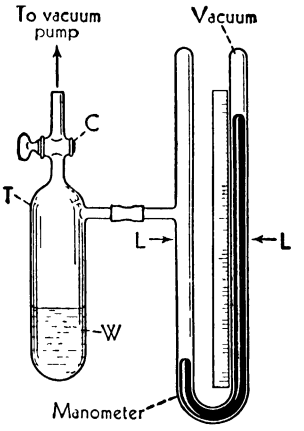


Fig. 11-3. Measurement of Vapor Pressure with a Manometer A liquid, say water, *W*, is placed in the tube, *T*, and the stopcock, *C*, is opened to a vacuum pump. If air and water vapor are pumped out of the system on the left-hand side of the U-tube, the two mercury levels will be *L*, *L*. Then if the stopcock is closed, the water evaporates and establishes an equilibrium vapor pressure at a given temperature. The difference in the level of the mercury columns indicates the vapor pressure of the liquid

the liquid was originally a vacuum or whether it contains air or any other gas. It is usually more convenient, however, to measure the vapor pressure with the liquid evaporating into a vacuum.

Measurement of vapor pressure. Experimentally the value of the vapor pressure of a liquid at any temperature may be measured in many different ways. The instrument most commonly used, the manometer, is illustrated in Fig. 11-3. Another simple method is as follows: Two barometers, with a Torricellian vacuum above the mercury column, are set up as shown in Fig. 11-4. A few drops of the liquid to be examined are introduced under the open end of *one* of the tubes. The liquid so introduced immediately rises to the top of the mercury column. Evaporation at once takes place, and, because of the pressure of the vapor so formed, the mercury column falls to some extent. When equilibrium is reached, the difference in level of the mercury in the two tubes (included between the dotted lines, *A* and *B*, in the figure) will measure the vapor pressure of the liquid in millimeters of mercury. The tubes may be surrounded by jackets through which heated liquids are circulated, to secure any desired temperature.

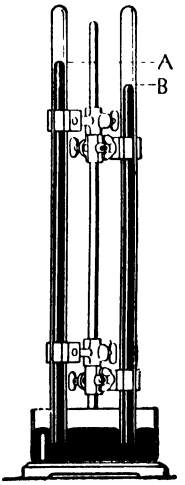


Fig. 11-4. Apparatus Used in Determining Vapor Pressure

Effect of Temperature upon Vapor Pressure · Measurements show that the vapor pressure increases sharply with rising temperature; and in Fig. 11-6 the experimental values of the vapor pressures of four liquids are plotted against temperature. How can this effect be explained?

Suppose we have a liquid in equilibrium with its vapor in an enclosed space. If the temperature is raised, the rate of evaporation will increase much more than will the rate of condensation. The average kinetic energy of the molecules in both the vapor and the liquid is increased. But the small fraction of the liquid molecules that have a kinetic energy far above the average, the "hot" molecules that are able to escape through the surface into the vapor, is markedly increased. Consequently, the rate of evaporation becomes temporarily greater than the rate of condensation, and the concentration of molecules in the vapor phase increases. As this increase takes place, however, the rate of condensation will begin to increase, and will shortly overtake the rate of evaporation, and establish a new equilibrium:

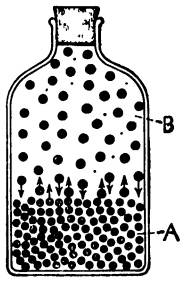


Fig. 11-5. Diagram of the Same Liquid as in Fig. 11-2 at a Higher Temperature

$$\text{Liquid} \rightleftarrows \text{vapor}$$

The concentration of vapor molecules and the vapor pressure will be higher than at the lower temperature (compare Figs. 11-2 and 11-5).

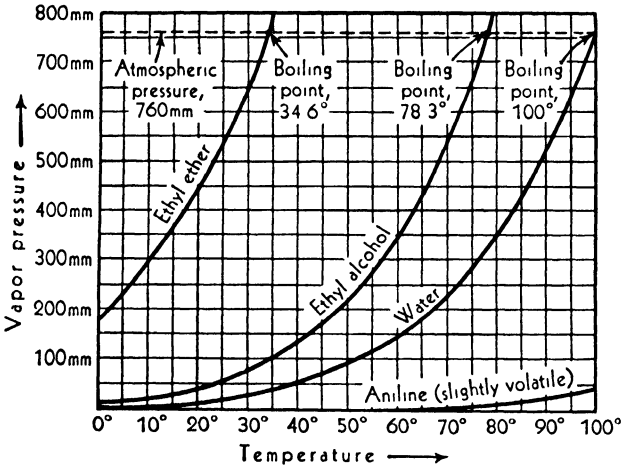


Fig. 11-6. Vapor-Pressure Curves, Showing Boiling Points of Several Liquids

Boiling Point · During the heating of a liquid at ordinary temperatures a portion of the energy given to it goes to raise its temperature, and a portion to change it into a vapor at its surface. When the pressure of the vapor arising from the liquid just exceeds the opposing atmospheric pressure, all the heat energy goes to change the liquid into vapor (in freeing the molecules from the attraction of their neighbors) and into mechanical work in pushing back the atmosphere. The temperature then remains constant, notwithstanding that heat is being applied to the liquid. This temperature is called the boiling point under the pressure in question. *The boiling point may be defined as the temperature at which the vapor pressure of the liquid just exceeds the opposing pressure of the atmosphere.* The boiling point at standard atmospheric pressure is often called the *normal* boiling point. By suitably altering the pressure on a liquid, it may be caused to boil at temperatures higher or lower than its normal boiling point. Thus, at high altitudes the boiling point of water is less than 100° (Fig. 11-7).

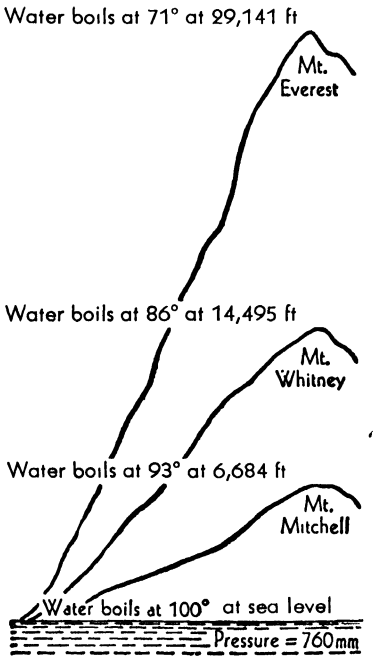


Fig. 11-7. Boiling Point of Water at Various Heights

Formation of Bubbles · We usually think of a liquid as boiling when bubbles form and rise freely through it, and this is really an accurate test, as will be seen by reference to Fig. 11-8. The figure represents a glass vessel in which water is being heated under an atmospheric pressure of 760 mm. When the whole body of water has been brought to a temperature of 100°, vapor escapes very rapidly from the surface. But the water in the interior or toward the bottom of the vessel, which is slightly superheated, does not wait until it comes to the surface but vaporizes where it is, and blows little bubbles with its vapor. In order that such a bubble, *B*, may form and survive, the pressure of the water vapor within the bubble must be a little greater than the hydrostatic pressure of the water lying above the bubble *plus the atmospheric pressure* transmitted by the water to the wall of the bubble. These bubbles, of course, rise to the surface as they are formed. Thus, the appearance of vapor bubbles (not to be confused with bubbles of dissolved air) in a heated liquid is a sure signal that the boiling point has been attained, that is, that the vapor pressure slightly exceeds the atmospheric pressure.

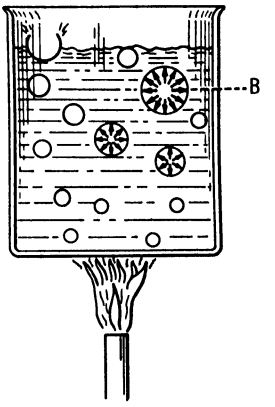


Fig. 11-8. Diagram Illustrating the Behavior of Bubbles in a Boiling Liquid

Volatility of Liquids · Liquids differ greatly among themselves in the magnitude of their vapor pressures at a given temperature. At ordinary temperatures some of them, such as ether, alcohol, and benzene, have a high vapor pressure and consequently a low boiling point. Such liquids are said to be *volatile*. They evaporate very rapidly when exposed to the open air. Other liquids, such as lubricating oils or mercury, have very low vapor pressures and correspondingly high boiling points.

Heat of Vaporization and Condensation · Since only the fastest-moving ("hottest") molecules in a liquid are able to escape through its surface, the liquid becomes colder when it loses these molecules. Heat must be supplied to maintain the evaporation. The quantity of heat absorbed in changing 1 g of a liquid into 1 g of vapor at constant temperature is called the *heat of vaporization*. The heat of vaporization of water at its boiling point is exceptionally large, amounting to 539 cal/g. Conversely, the condensation of a gas or vapor to a liquid liberates a quantity of heat exactly equal to the heat of vaporization. This is called the *heat of condensation*.

Critical Points · In the early days of experimentation with gases, there were no satisfactory methods for storing or transporting any considerable

quantity of a gas, and investigators found it necessary to generate and purify the gases as they were needed for their researches. At the present time it is possible to purchase a large number of remarkably pure gases, such as nitrogen, oxygen, hydrogen, carbon dioxide, sulfur dioxide, and ammonia. These are supplied in highly compressed form in strong steel cylinders fitted with suitable valves and couplings. If we could equip tanks of these gases with small windows so that we could see the contents, we should learn a rather startling fact. The tanks of oxygen, nitrogen, and hydrogen contain nothing but highly compressed gas, while those of carbon dioxide, sulfur dioxide, and ammonia contain *liquid* as well as gas. How can we account for this difference in behavior in the two groups of gases?

To find an answer to this question let us approach the problem from a somewhat different angle. If a liquid is sealed within a tube, *A* (Fig. 11-9), from which all air has been withdrawn, the lower end of the tube will be filled with liquid and the upper end will contain vapor. If the liquid is now heated gently, more and more of it is vaporized, and the pressure in the confined space increases rapidly. The density of the remaining liquid diminishes, and the density of the vapor increases. At some temperature the two will become identical, and the boundary line between them, *B* (the *meniscus*), will fade out. The temperature at which this occurs is called the *critical temperature*, and the pressure exerted by the vapor at this temperature is the *critical pressure*. One may say that *the critical temperature of a gas is the temperature above which that gas cannot be liquefied, no matter how great a pressure is applied.* The critical pressure is that pressure which at the critical temperature just serves to liquefy the gas. The critical temperatures and pressures of a few gases are given in the following table:

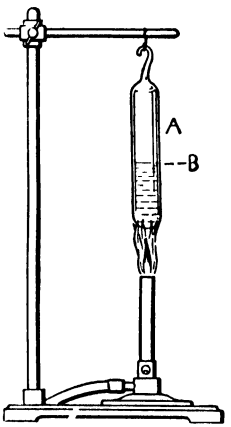


Fig. 11-9. Drawing Illustrating the Critical Temperature of a Liquid

CRITICAL TEMPERATURES AND PRESSURES

GAS	MELTING POINT	BOILING POINT	CRITICAL TEMPERATURE	CRITICAL PRESSURE IN ATMOSPHERES
Hydrogen . .	− 259.1°	− 252.7°	− 239.9°	12.8
Nitrogen . .	− 209.8°	− 195.8°	− 147.1°	33.5
Oxygen . . .	− 218.4°	− 183.0°	− 118.8°	49.7
Sulfur dioxide	− 75.5°	− 10.0°	157.2°	77.7
Ammonia . .	− 77.7°	− 33.3°	132.4°	111.5
Water . . .	0.0°	100.0°	374.0°	217.7
Carbon dioxide	− 56.6°	(Sublimes at − 78.5°)	31.1°	73.0

Critical Temperature and Molecular Behavior · We have previously seen that it is the attractive forces between molecules which bind them in the liquid state and produce such effects as surface tension. With rising temperature the average speed of the molecules in a liquid increases. If the speed becomes great enough (high temperature), there will come a point (critical temperature) where the attractive forces are entirely overcome by the increased speed, and there can be no liquid, even if the gas is compressed into a space no larger than a liquid would occupy.

Liquefaction of gases—historical. The earliest systematic efforts at liquefaction of gases were those of the English scientist Faraday (Fig. 13-1), about 1823. He relied upon the effect of pressure, together with moderate cooling, and most of his experiments were carried out in the following way: A quantity of solid material which, when heated, would liberate a considerable quantity of the gas to be liquefied was placed in one end of a bent tube. The other end was sealed and the tube arranged as shown in Fig. 11-10. *A* is the solid material and *B* a cooling bath of ice water. When the solid is heated, the gas is given off in a confined space and, being under great pressure, liquefies in the cold portion of the tube. In this general way Faraday liquefied a number of gases, such as chlorine, ammonia, and carbon dioxide. He was unable to liquefy other gases by this method and called these permanent gases.

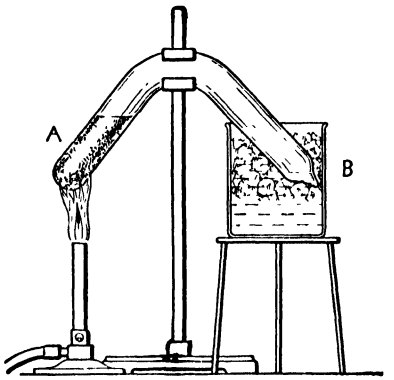


Fig. 11-10. Faraday's Method for Liquefying Gases

Liquefaction of Gases · If the critical temperature of a gas is somewhat above ordinary temperatures, the gas can be liquefied by pressure alone. For example, at 20° carbon dioxide (critical temperature 31.1°) is liquefied by a pressure of 56.3 atm. With gases of low critical temperatures the difficulty lies in securing the low temperature, since the requisite pressure is readily available. In modern practice *the gas is made to cool itself* by purely mechanical methods. One of the procedures is based on the following principle: Most compressed gases become cooled when *throttled* to a lower pressure, that is, when allowed to escape through a small opening or a nozzle from a higher to a lower pressure. This cooling is known as the Joule-Thomson effect, and is to be explained in terms of the attractive forces between the gas molecules. When the molecules of the compressed gas move apart into a larger volume at the lower pressure,

they separate from one another against the attractive forces holding them together. To accomplish this work of separation requires energy.

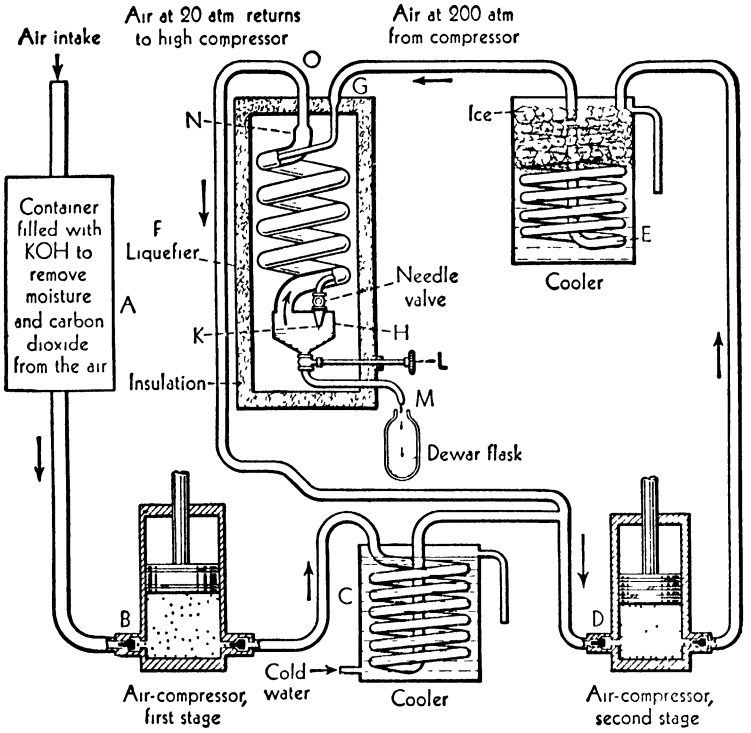


Fig. 11-11. The Steps in the Liquefaction of Air The air enters the apparatus at the air intake and passes through the chamber, *A*, filled with absorbents for moisture and carbon dioxide. It then enters the air-compressor *B*, where it is highly compressed. Heat is evolved in this process, and the compressed hot air is cooled by cold water in the cooler, *C*. It undergoes further compression in *D* and is again cooled in *E*. The highly compressed cold air then enters the liquefier, *F*. Inside the liquefier the copper tube, *G*, is enclosed in a tube, *V*, of larger diameter, and the two concentric tubes form a spiral. At *K* there is a very small opening, controlled by a needle valve. Through this hole some of the compressed air escapes into the cup, *H*, and expands to a lower pressure. In expanding, the air becomes very cold, and is led back through the outer tube, *N*, to cool the incoming air within the inner tube, *G*. As the process continues, the air in tube *G* becomes increasingly cold until it reaches the temperature of liquefaction, when drops of liquid air form and collect in the cup, *H*. By means of the valve, *L*, the liquid air is drawn off into the Dewar flask through *M*. The cold, expanded air returns to the compressor *D* through the pipe *O*.

This energy is taken from the heat energy of the gas itself; consequently the gas is cooled. If now this cold gas is allowed to flow back over the compression vessel, the compressed gas may become so cold that, after the still further cooling produced by the throttling, it will liquefy. The details of the liquefaction of air by this method are shown in Fig. 11-11.

Dewar Flasks · For collecting and temporarily preserving such liquids as liquid air, whose boiling point is far below the temperature of an ordinary room, it is essential that the container be well insulated. Dewar flasks (Fig. 5-8, p. 50) are employed for this purpose. Liquid air may be preserved in such a vessel for many hours. Thermos bottles of the same plan of construction are now familiar utensils for keeping liquids either hot or cold, and are very effective.

Mechanical Refrigeration; Ice Machines · Mechanical refrigerators (Fig. 11-12) and ice-making machines all utilize the cooling effect of ex-

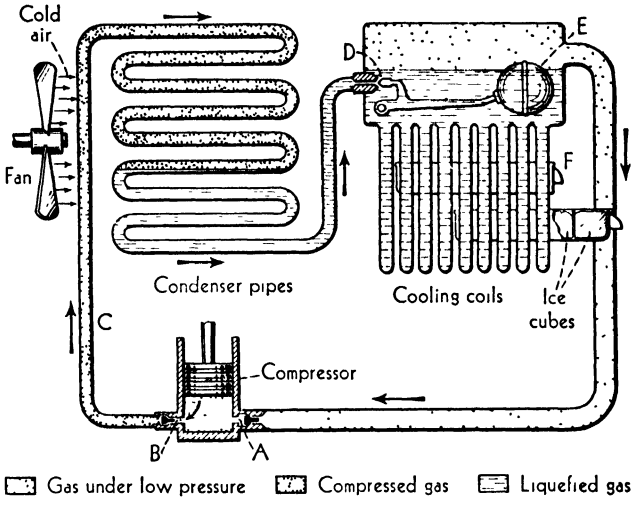


Fig. 11-12. Diagram to Show How the Electric Household Refrigerator Operates The gas used enters the compressor at valve *A*. The compressed gas is forced through valve *B* into the pipe *C*, is cooled by the fan, or in a radiator, and liquefies in the condenser pipes. The liquid then enters the freezing compartment at *D*, where it evaporates, cooling the liquid in the coils to a low temperature. The evaporated gas returns to the compressor. The float-valve, *E*, gradually falls as the liquid evaporates, thus allowing more of the liquid to enter the freezing compartment at *D*. The valve rises with the surface of the liquid, being adjusted so as again to close the pipe at *D* when the desired volume of the liquid has been admitted

panding gases and the absorption of heat by the vaporization of low-boiling liquids. The two important economic factors are (1) the relative ease of compression to the liquid state and (2) the magnitude of the heat of vaporization. In small domestic refrigerators, sulfur dioxide, formerly used almost entirely, is now being replaced by dichlorodifluoromethane (CCl_2F_2) and related compounds, which are odorless and nontoxic. For cold-storage rooms and ice machines ammonia is largely used.

The table on page 178 gives the significant constants for some of the gases that have been or are being used in refrigeration.

PROPERTIES OF REFRIGERANT GASES

GAS	CRITICAL TEMPERATURE	CRITICAL PRESSURE	BOILING POINT	HEAT OF VAPORIZATION (Calories per Gram)		
				− 10°	0°	10°
Ammonia (NH_3)	132.4°	111.5	− 33.3°	309.9	301.8	293.1
Carbon dioxide (CO_2) . .	31.1°	73	—	62.67	56.15	48.5
Sulfur dioxide (SO_2) . . .	157.2°	77.7	− 10.0°	94.9	91.2	88.7
Methyl chloride (CH_3Cl) .	143°	66	− 23.7°	98.5	96.9	95.1
Ethyl chloride (C_2H_5Cl) .	187.2°	52	12.2°	95.5	93.9	92.0
Dichlorodifluoromethane, or Freon (CCl_2F_2)	111.5°	39.56	− 29.8°	38.6 at − 15°	—	33.1 at 30°

Transition between Solids and Liquids or Gases

Solid Substances · When a liquid substance is cooled, it becomes less and less fluid. At a sufficiently low temperature all liquids become rigid, and we call this form a *solid*. As a rule, the change from liquid to solid is sudden. At some definite temperature small crystals begin to form, and the temperature of the liquid comes to a *perfectly definite value* called the *freezing point*; and this remains unchanged until all the liquid has solidified. For example, water solidifies, or freezes, at 0°. Solids formed in this way are always *crystalline*; and this indicates an orderly arrangement of particles within the solid. Occasionally there is no definite point of solidification, and the changes from the liquid state into that of a rigid substance are gradual. Glasses, glazes, glue, tar, and gums are examples of such materials. These are sometimes called *amorphous solids*, to distinguish them from crystalline solids; but it is better to consider them as still liquid but so viscous that they are almost as rigid as crystalline solids.

Freezing Point and Melting Point · When a crystallizable liquid, such as water, is cooled, it does not always *begin* to crystallize at its freezing point. Indeed, liquid water has been cooled far below 0° without freezing. A liquid below its freezing point is said to be *undercooled*. If a crystal of the substance once forms, or if a "seed crystal" is dropped into the undercooled liquid, solidification at once begins, heat is given out in the process, and the temperature rises to the true freezing point and remains there as long as both liquid and solid are present. *The freezing point is defined as the temperature at which both solid and liquid will remain in contact with*

each other without change of temperature. The more viscous a liquid is at its freezing point, the more readily undercooling takes place; and with very viscous liquids, as we have seen, true solidification may never occur.

Conversely, when a crystalline solid is slowly heated, its temperature steadily rises to a certain definite point (unless the solid should undergo decomposition). Further application of heat does not raise the temperature, but the solid begins to melt. If the substance is pure, the temperature remains constant until the melting is complete, and then rises again. While the solid and liquid are in contact with each other, in *equilibrium*,

$$\text{Solid} \rightleftarrows \text{liquid}$$

the addition of heat energy will cause the solid to change to liquid (at the melting point), and the removal of heat will result in the conversion of the liquid to solid (at the freezing point). Obviously the temperature of the melting point and that of the freezing point are identical.

Heat of Fusion and of Solidification · The heat energy supplied to a substance during the process of melting has no effect on the temperature, but is used up in altering the physical state of the substance. The heat absorbed in converting 1 g of a solid at its melting point into 1 g of liquid at the same temperature is called the *heat of fusion* of the substance. For ice this amounts to about 80 cal. The heat given out when 1 g of a liquid at its freezing point solidifies to 1 g of solid is called the *heat of solidification.* The heat of solidification is the same in quantity as the heat of fusion, and represents the difference in energy between the orderly, rigid arrangement of molecules in a solid and the relative disorder and mobility of molecules in a liquid.

Vapor Pressure of Solids · Many solids give off vapor at ordinary temperatures, just as liquids do. This is evident from the odor of such solids as camphor and naphthalene (moth balls). Here, again, an equilibrium exists, between the solid and the vapor:

$$\text{Solid} \rightleftarrows \text{vapor}$$

As the temperature is raised, the pressure of the vapor, or the *vapor pressure* as we call it, increases. If it increases to the point where it just exceeds the pressure of the atmosphere, the solid cannot be heated to a higher temperature in an open vessel, just as a liquid cannot be heated (at the pressure of the atmosphere) above its boiling point. To melt such a solid it is necessary to heat it in a closed vessel. This behavior is illustrated by solid carbon dioxide, whose vapor pressure reaches 760 mm at $-78.5°$, but which does not melt until $-56.6°$. At this latter point its vapor pressure is more than 5 atm. When the vapors from such solids are cooled, they pass directly back into the solid form. The process of

converting a solid into a vapor and condensing the vapor to a solid again is called *sublimation*, and the solid is said to *sublime* on heating. The corresponding process with liquids is called *distillation*. Solids which have a sufficient vapor pressure are often separated from nonvolatile impurities by sublimation, and this practice is the origin of such names as *corrosive sublimate* (mercuric chloride).

Equilibrium diagram. In the preceding pages we have seen that a number of different types of equilibrium exist in a system containing a substance in different physical states. Thus, with water we have an equilibrium between the vapor and the liquid; between the vapor and the solid; between the liquid and the solid. We can show the general character of these three equilibria in a very compact form in a diagram (Fig. 11-13) in which we represent temperature along the horizontal axis and pressure along the vertical axis. The curve OA is a plot of the experimentally measured vapor pressures of the liquid over a range of temperatures—for example, the vapor pressure p_1 at temperature t_1, and p_2 at t_2. This curve ends at a point, A, which is the critical temperature, above which the substance can no longer exist in the liquid state. OB is the vapor-pressure curve of the solid, usually called the sublimation curve. The point O, where these two curves intersect, is the freezing point of the liquid; and at that point the vapor pressures of solid and liquid are equal. Since the two curves intersect at this point, the solid, liquid, and vapor can coexist at this temperature and pressure; but they can do so at no other point. If no solid makes its appearance at the freezing point, the vapor pressure of the liquid will be represented by the extension of the curve AO toward S. It will be seen that the vapor pressure of such an undercooled liquid is greater than that of the solid at the same temperature, as at t. This indicates that the undercooled liquid is in a more unstable condition. Very few (if any) solids can be heated above the melting point without melting; so the curve BO can rarely be prolonged beyond the melting point, as at X in the figure.

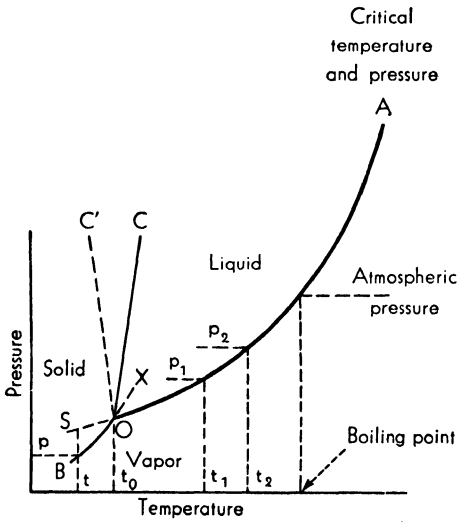


Fig. 11-13. Diagram Illustrating the Equilibria of the Three States of Matter

If, when the solid and liquid and vapor are all in equilibrium, at the point O (often called the *triple point*), one applies a steady outside pressure, as with a piston, greater than the pressure of the vapor (Fig. 11-14), the vapor will all condense and solid and liquid alone remain. Then, if the applied pressure is increased

more and more (Fig. 11-15), the result is that the freezing point, or melting point, is raised for all known substances (with two or three exceptions). This effect is indicated by the line *OC* (Fig. 11-13), which represents the equilibrium between melting solid and freezing liquid.

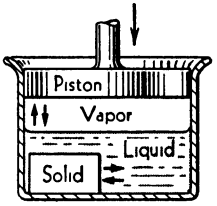


Fig. 11-14

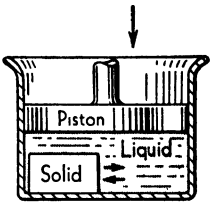


Fig 11-15

The Principle of Le Châtelier · An equilibrium, once established, tends to maintain itself indefinitely if it is not disturbed from the outside; if it is so disturbed, by various kinds of forces, stresses, or changes in the environment, it may be shifted. There is a far-reaching generalization, called the principle of Le Châtelier, which deals with changes in an equilibrium of any sort, either chemical or physical. Le Châtelier's principle may be stated as follows: *If a stress is brought to bear upon a system at equilibrium, the position of equilibrium will shift in such a way as to diminish the stress so applied.* This principle is extremely helpful because it allows us to predict what will happen to an equilibrium when it is disturbed.

Illustrations of Le Châtelier's Principle · To show how the predictions are made, let us take the equilibria that we have just been discussing.

1. **Liquid $\rightleftarrows$ vapor.** A given mass of a substance occupies a larger volume as a vapor than as a liquid; and under an applied pressure the volume of vapor will shrink, and the vapor will condense and so tend to relieve the stress. The equilibrium will shift toward the left, that is, from the vapor to the liquid. But if the outside pressure is lowered below the vapor pressure, the equilibrium will shift the other way, and the liquid will evaporate. If the temperature is raised by putting heat into the system, the equilibrium will shift in such a way as to absorb the heat; this means that the net result will be an evaporation of the liquid and an increase in the vapor pressure at the new equilibrium, at the higher temperature.

2. **Solid $\rightleftarrows$ vapor.** Here the same sort of predictions are made, and the same actual changes in equilibrium observed, as in 1.

3. **Solid $\rightleftarrows$ liquid.** Since, in practically all known instances, the density of a liquid is less than that of the solid (when the two are in equilibrium) and its volume greater, an applied pressure will tend to drive the liquid over into the solid state. Hence it becomes more difficult to melt the solid under an applied pressure, and the melting point is raised; the

freezing point (the same temperature as the melting point) is more easily reached as one cools the liquid down for freezing.

Exceptions · However, the all-important substance *water* has a smaller density and larger volume in the solid state than in the liquid state. Ice floats. Consequently the melting point and freezing point are lowered by applied pressure, as indicated by the line OC' in Fig. 11-13. Another substance that possesses this extremely unusual property of expanding in the act of solidification is bismuth (Chap. 23).

Crystal Structure

Crystals · When a liquid freezes, it changes into a mass of solid bodies, which have a definite geometric form and are called crystals. Similar bodies may also be deposited from solutions or be formed by condensing vapors. A crystal is always bounded by plane surfaces, which are arranged in an orderly fashion with reference to imaginary lines drawn through the crystal and called its *axes*. Every crystal has therefore a definite geometric form. While the variety of form which crystals may assume is almost endless, it has been found that crystals may all be referred to one of *six fundamental arrangements* of axes, which are known as the six *crystallographic systems*. These arrangements, together with two of the simplest crystal forms in each system, are shown in the accompanying figures (Figs. 11-16 to 11-22).

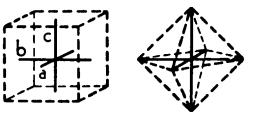


Fig. 11-16. Isometric System · A cube (*A*) and a regular octahedron (*B*) are two of the several forms that may be built on the axes of this system

The crystal systems. The relation of the axes in the several systems is as follows:

1. Isometric, or regular, system (Fig. 11-16); three equal axes, all at right angles to each other.
2. Tetragonal system (Fig. 11-17): two equal axes and a third of different length, all at right angles.
3. Orthorhombic system (Fig. 11-18): three unequal axes, all at right angles.
4. Monoclinic system (Fig. 11-19): two axes at right angles and a third at right angles to one of these but inclined toward the other. The axes may be of any relative lengths, and the angle of inclination may vary from 0° to 90°.

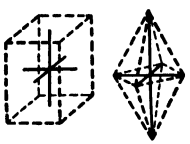


Fig. 11-17. Tetragonal System

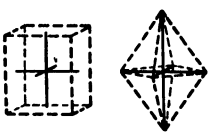


Fig. 11-18. Orthorhombic System

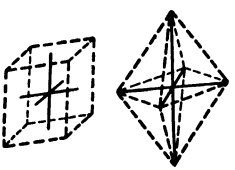


Fig. 11-19. Monoclinic System

5 Triclinic system (Fig. 11-20): three axes, all inclined toward each other. The axes may be of any relative lengths, and the angles of inclination may also vary.

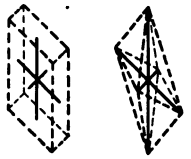


Fig. 11-20. Triclinic System

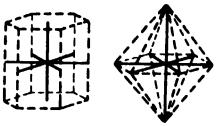


Fig. 11-21. Hexagonal System



Fig. 11-22. Hexagonal System (Rhombohedral Form)

6. Hexagonal system (Fig. 11-21): three equal axes in the same plane, intersecting at angles of 60°, and a fourth at right angles to all of these. In addition to the two general forms shown in Fig. 11-21 there are many forms belonging to this system, such as the rhombohedral form represented in Fig. 11-22.

Crystal Form a Characteristic of a Substance · In general, under the same conditions, a given substance will always crystallize in a *form* which may be referred to the same system, with the same ratio of axis lengths and degree of inclination. The actual crystal *shape* may be quite different, however. For example, it may be either a cube or an octahedron, both of which are forms in the isometric system. Two different substances which crystallize in the same form or almost the same form are said to be *isomorphous.*

Allotropic Forms · It is evident that the atoms composing an element or present in a compound might find it possible to arrange themselves in either of two (or more) patterns, just as we can pile oranges in two patterns by starting with a square base for one pile and a hexagonal base for the other. This would give rise to different crystalline forms with different physical properties and different chemical energies. This is actually observed to happen with a great many substances, both elements and compounds, and these modifications are called *allotropic forms.* For example, the diamond is carbon crystallized in the isometric system, while graphite is carbon crystallized in the hexagonal system.

A substance that crystallizes in two different systems is said to be *dimorphous.* For example, one form may occur when the substance freezes, and another when it is deposited from solution. *Trimorphous* substances are also known.

The Crystal Lattice · Like gases and liquids, crystals are made up of particles of matter, namely, of atoms, ions, or molecules. The shape of a crystal is the consequence of the spatial arrangement of the particles within the body of the crystal. The very fact that every crystalline sub-

stance possesses a characteristic form must necessarily mean that its constituent particles always marshal themselves in space in a perfectly definite and always-repeated manner. Such an ordered array of particles in three-dimensional space is called a *crystal lattice* or oftentimes a *space lattice*. A very familiar illustration of what is meant by a space lattice is shown in Fig 11-23. This particular method of piling spheres together is employed by grocers in displaying their apples, oranges, and grapefruit; and one may often see cannon balls piled up in this fashion in old courthouse yards.

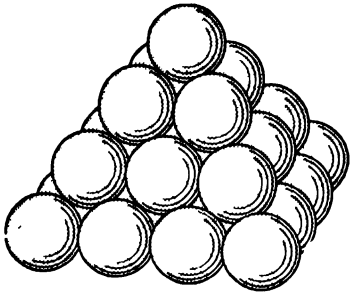


Fig. 11-23. A Crystal Lattice

If the particles in a crystal are in fact arranged in an orderly way, then it should be possible to draw many sets of planes through the particles. Certain of these planes will be parallel, such as the two horizontal planes shown in Fig. 11-25, and these will all be the same distance apart. When a beam of light falls upon such a layered arrangement, reflection occurs at certain angles of incidence, depending upon the distances between the layers, and upon the wave length of the light. The German physicist Laue suggested in 1912 that X rays, discovered by Roentgen nearly twenty years earlier, might have a wave length of about the proper size for reflection. This was found to be the case, and Laue, Bragg, and others perfected this use of X rays for determining the distances be-

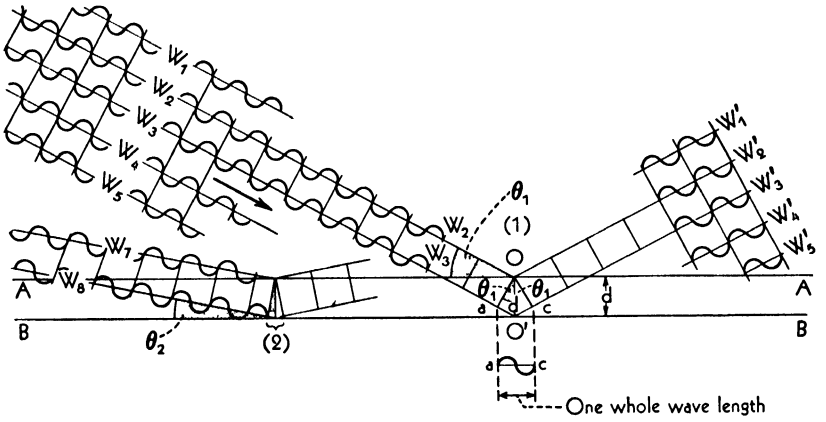


Fig. 11-24. Two Layers of a Crystal Showing an X-ray beam of a single wave length reflected by a crystal at angle θ_1 at (1); another reflected at angle θ_2 at (2)

tween particle planes in crystals. Since X rays cannot be detected by the eye, a photographic plate or film is used to record the position of the reflected beam.

The Bragg Method · Suppose we have a beam of X rays of a single wave length falling upon a crystal. The beam is shown in section at $W_1W_2W_3W_4W_5$ in Fig. 11-24, and consists of many separate waves marching along together in step, or in phase, crest falling upon crest and trough upon trough, as the wave front advances. The total strength or intensity of the beam is the sum of the intensities of all the individual waves, since they are all in step with one another.

Suppose the angle the beam makes with the set of parallel planes AA, BB is θ_1, as shown at (1) in the figure. The angle θ_1 at which the incident beam strikes the surface will also be the angle at which the beam is reflected, $\theta_1 = \theta_1$, and the beam, only a part of which is reflected from the first layer, will penetrate to deeper and deeper layers, and be partly reflected successively from each of them, always at angle θ_1. The reflected portions will rejoin and form the issuing beam, $W'_1W'_2W'_3W'_4W'_5$.

To simplify matters let us focus our attention on two of the waves, W_2 and W_3; and let us show the advancing wave front at stages one wave length apart. Wave W_2 is reflected at O from the first layer, AA. Wave W_3, as it penetrates down to the second layer, BB, and is reflected at O', must obviously travel a greater distance than wave W_2. The distance is greater by the amount $aO'c$; and if this extra distance is exactly equal to one wave length, then in the issuing beam wave W'_3 will lag behind wave W'_2 by just one wave length, and the two waves will still be in phase, and will co-operate in producing a maximum intensity.

In the experiment represented at (1) in the figure, the angle θ_1 at which the oncoming beam strikes the surface, has been so chosen that $aO'c$ is equal to one wave length. But if, as at (2), the angle (which we may call θ_2) is made much smaller, the extra distance (corresponding to $aO'c$) becomes much smaller than a wave length. In the reflected beam the pair of waves W_7 and W_8 will therefore not be in step. Interference between troughs and crests occurs, rather than reinforcement; and the reflected beam may undergo considerable reduction in its intensity, or even be blotted out.

Determination of the Distance between Reflecting Planes · We have just seen that reinforcement occurs in the reflected beam if the extra distance $aO'c$ is equal to one whole wave length; or $aO'c = (wl)$, where (wl) represents wave length. We may now express the distance $aO'c$ in terms of d, the distance between the large planes:

The angle aOO' is equal to θ_1.

The sine of angle $\theta_1 = \dfrac{aO'}{d}$.

Therefore the distance $aO' = d \sin \theta_1$.

But the distance $aO'c = 2d \sin \theta_1$.

And $2d \sin \theta_1 = (wl)$ when the waves reinforce one another.

Consequently, if one knows (wl) for the X ray, and by experiment can determine the angle θ_1 at which the intensity of the reflected beam is at a maximum, one can then calculate d, the only unknown quantity in the equation; d is the distance between the regularly spaced reflecting layers.

Working Out a Space Lattice · Let us, then, allow a beam of monochromatic X rays to fall at an angle on a face of a cubic (isometric) crystal with a piling of atoms as in Figs. 11-23 and 11-29, and determine the interlayer distance of the set of layers parallel to this face. We then turn the crystal through an angle of 90° and determine the interlayer distance for planes perpendicular to the first set, and finally we go through the same procedure for the other set of layers perpendicular to the first two. In this way we determine the spacing of three sets of planes, all at right angles to one another, as shown in Fig. 11-25. Since all these planes are populated with atoms, it follows that the points at which the three mutually perpendicular planes intersect will be occupied by atoms. Consequently we are able to mark out, by this method, the location of the atoms and hence determine the structure of the lattice.

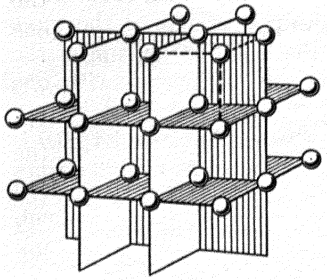


Fig. 11-25. Mutually Perpendicular Intersecting Planes

For a cubic crystal these three distances are found to be the same, and thus the crystal is made up of small cubes. This result confirms something that was suspected long before X rays were discovered, namely, that a crystal is built up from small blocks, or *unit cells*, belonging to the same crystallographic system as the crystal itself.

The Laue Method · In the Laue method a pencil-like beam of X rays, of many wave lengths, enters the crystal perpendicular to a face, passes directly through, and is caught on a photographic plate on the other side of the crystal. Many sets of lattice planes at various angles to the central X-ray beam (on its way through the crystal), and cutting across the path of the beam, co-operate with one another to reflect the X rays and to produce a pattern of reinforcement spots on the photographic plate. Over all the rest of the photograph, interference blots out the X rays. Fig. 11-26 shows a Laue photograph of magnesium oxide. From the position of the spots and their size one can calculate the position of the intersecting lattice planes, and work out the position of the atoms in the lattice.

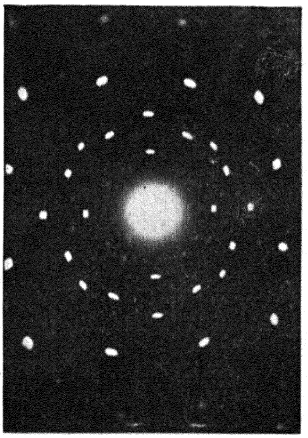


Fig. 11-26. Laue Photograph of Magnesium Oxide

Results of X-Ray Analysis · The lattice structures of a great many crystals have been solved by means of X-ray analysis, and we may now

glance at a few of the very simple ones. Others will be presented in connection with the appropriate compounds or elements.

Sodium chloride. Fig. 11-27 shows a diagram of the crystal lattice of sodium chloride. The lattice is made up not of *molecules of sodium chloride* nor of *atoms of sodium* and *atoms of chlorine*, but of *sodium ions* and *chlorine ions*, that is, electrically charged atoms. In the lattice every sodium ion is surrounded by six chlorine ions: one above, one below, one in front, one behind, one to the left, one to the right. Likewise every chlorine ion is surrounded by six sodium ions.

Fig. 11-27 gives only the position of the centers of the sodium and chlorine ions. These ions are not as small, nor are they separated from

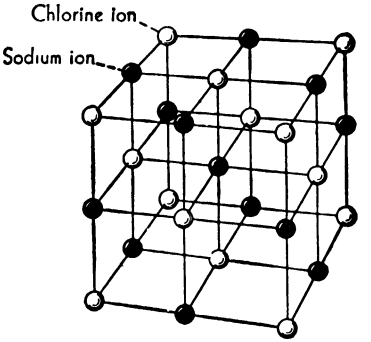


Fig. 11-27. Diagram of the Crystal Lattice of Sodium Chloride

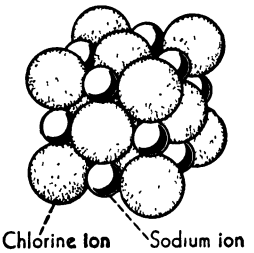


Fig. 11-28. Crystal Lattice of Sodium Chloride

one another as far, as one might conclude from Fig. 11-27. The ions are probably actually "touching" one another, and Fig. 11-28 portrays the situation more satisfactorily and also indicates the relative sizes of the two ions.

The conclusion that this lattice is made up of ions rather than of atoms is based upon measurements of the intensities of the reflected X-ray beam. The intensity depends upon the number of electrons in the atoms or ions in the crystal planes and corresponds in sodium chloride to units containing 10 electrons and 18 electrons respectively, that is, ions of sodium and chlorine, rather than atoms, which would contain 11 electrons and 17 electrons (p. 39).

Copper, silver, gold · The crystal lattices of metals are made up of *atoms*, not *ions*. The atoms of such metals as copper, silver, and gold are arranged in the lattice as shown in Fig. 11-29. The main difference is that the three metals have atoms of different sizes. This type of lattice structure is called the *face-centered cubic*. Inspection of Fig. 11-29 will show that the lattice may be divided into little cubes. There is an

atom in the center of every face of these cubes (as well as an atom at every one of the four corners of the face); hence the name. As a matter of fact, the face-centered cubic lattice is exactly the same as that of Fig. 11-23 (the groceryman's method of piling up spheres), although there the pile is viewed from a position different from that in Fig. 11-29.

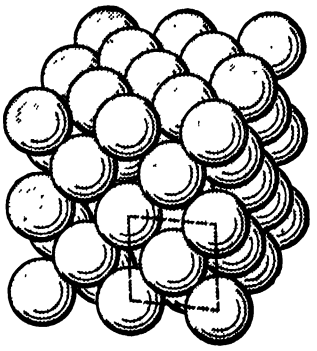


Fig. 11-29. Face-centered Cubic Lattice

The Scope of X-Ray Analysis · It will be seen that X-ray analysis gives us a wonderful insight into the fundamental make-up of solid matter. This in turn throws much light upon the properties of matter *in bulk*, such as malleability, ductility, electrical conductivity, hardness, magnetic effects, solubility, melting point, allotropic changes, and many others. It enables us to investigate the way in which many materials of everyday life are put together, and aids us in understanding the properties of natural minerals, alloys, the silicates, rubber, cellulose, muscle tissue, hair, bone, teeth, and hundreds of other materials.

QUESTIONS

1. Define (*a*) *vapor pressure*; (*b*) *boiling point;* (*c*) *critical temperature;* (*d*) *heat of vaporization;* (*e*) *melting point;* (*f*) *heat of fusion;* (*g*) *sublimation.*

2. What is meant by (*a*) *volatility;* (*b*) a *vapor-pressure curve;* (*c*) a *triple point;* (*d*) an *equilibrium*?

3. Give a clear picture, in terms of the kinetic-molecular theory, of the processes of (*a*) evaporation; (*b*) condensation; (*c*) melting; (*d*) freezing; (*e*) sublimation.

4. (*a*) State Le Châtelier's principle. (*b*) With it explain why the freezing point of water is lowered by applied pressure. (*c*) Why is water exceptional in this respect? (*d*) Why does the vapor pressure of a liquid increase with rising temperature?

5. (*a*) Why does the melting point of a solid remain constant, even while heat is being added to the solid? (*b*) Why does the temperature of a liquid remain constant while the liquid is boiling?

6. What is meant by the following terms: (*a*) *crystal lattice;* (*b*) *amorphous solid;* (*c*) *isomorphous crystals;* (*d*) *allotropic form;* (*e*) *crystallographic system*?

7. (*a*) Explain how a mechanical refrigerator operates. (*b*) What properties must be considered in choosing a substance which will be a good refrigerant?

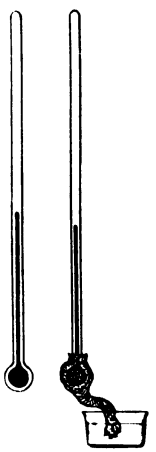


Fig. 11-30

8. A cylinder equipped with a piston contains water and no other substance. In what states will the water be present under the following conditions: (*a*) pressure 50 mm, temperature 10°; (*b*) pressure 760 mm, temperature 99°; (*c*) pressure 760 mm, temperature 101°; (*d*) pressure 220 atm, temperature 350°; (*e*) pressure 220 atm, temperature 380°; (*f*) pressure 500 atm, temperature 380°?

9. Outline the reasoning which leads to the conclusion that the vapor pressures of the solid and liquid forms of a substance must be equal at the melting point (see Fig. 11-13).

10. Is the vapor pressure of a liquid independent of (*a*) the amount of liquid present; (*b*) the size of the enclosure above the liquid; (*c*) the extent of surface of the liquid; (*d*) the nature of the liquid? Give reasons for your answers.

11. Suppose that one of two thermometers (Fig. 11-30) has its bulb wrapped with a piece of cloth which is kept moist (end of cloth dips into water—see the figure). (*a*) Which thermometer should register the lower temperature, and why? (*b*) What useful application can be made of such an arrangement?

PROBLEMS

1. How many calories of heat would be absorbed in melting 1 lb of ice at 0° to water at 0°?

2. How much sulfur dioxide at its boiling point must be vaporized in order to cool 800 g of water from 20°, and freeze it in the freezing compartment of a refrigerator? (Assume that there is no loss of heat to the outside.)

3. If 100 g of ice at 0° and 100 g of water at 100° are mixed in an insulated container, what will be the state and temperature of the system after equilibrium has been attained?

4. A quantity of oxygen was collected over water at a temperature of 27° and a pressure of 737 mm. What volume would this oxygen occupy in the dry state, under standard conditions?

5. A certain evacuated container which is held at a temperature of 29° becomes just saturated with water vapor when 1 g of water, placed in it, evaporates completely. What is the volume of the container?

6. Assume that 6.02×10^{23} molecules of liquid water at 100° occupy a volume of 18 ml, and 6.02×10^{23} molecules of water vapor at 100° occupy a volume of 30,600 ml. Calculate the average distances between the molecules, center to center, in the two states.

7. What is the weight of the water present in a liter of air saturated with water vapor, at 30°?

8. How many water molecules are there in 1 ml of liquid water at 4°?

CHAPTER 12

SOLUTIONS

A solution may be properly defined as a homogeneous mixture. This means that a solution is of such even quality throughout that its parts cannot be distinguished even with the most powerful optical microscope. A solution is a mixture of particles which may be atoms, ions, or molecules.

Why Does a Substance Dissolve? The passage of a substance into solution somewhat resembles evaporation (Chap. 11). But the solution process differs from evaporation in one respect. In evaporation the vapor space does not attract the particles of the evaporating substance; the particles of a dissolving substance *are* attracted by the molecules of a solvent. These attractive forces may be van der Waals forces, of various strength, such as those that cause deviations from the gas laws (Chaps. 6, 11), or they may be the very strong forces which produce chemical combination. If these attractive forces of the solvent are strong enough to overcome the attractive forces that hold the particles of the solute together, the substance will dissolve. As a rule, substances of very high melting point, whose particles are bound very rigidly together, do not dissolve appreciably in a solvent. Examples are silica, the heavy-metal silicates, barium sulfate, calcium carbonate, and the heavy-metal sulfides. The ions of some compounds, even though they are bound very tightly together, have such a strong attraction for water molecules that they become jacketed, or *hydrated*, or *solvated*, by water molecules; hence they dissolve. Examples of such compounds are sodium chloride, calcium chloride, potassium nitrate, and copper sulfate.

Oil and water proverbially do not mix, or dissolve in each other. Probably water does not dissolve in oil because water molecules attract one another so strongly that they will not respond to the much feebler attraction of the oil molecules for them; nor will the water molecules, because of this strong attraction, separate from one another far enough to allow the oil molecules to penetrate among them.

There are no very satisfactory generalizations that can be made about why a substance dissolves. There may be some truth in the old rule that "like dissolves like." Oil molecules are usually made up largely of carbon and hydrogen atoms. Even if they will not dissolve in water they will dissolve in various hydrocarbon solvents; and if the oil molecules are

made to combine with enough oxygen atoms, like the ethane molecules discussed on page 168, they can come to be enough like water so that they will dissolve in water.

Constituents and Varieties of Solutions · One constituent of a solution (usually the more abundant one) we think of as the medium in which the other (less abundant) constituent is dissolved; the medium we call the *solvent*, the dissolved constituent the *solute*. Since, before the solution is made, the solvent-to-be and the solute-to-be can each be either a gas, liquid, or solid, we see that there are nine possible combinations (3×3), or nine general kinds of solutions possible. Five of the most important pairs will now be considered.

Solutions of Gases in Gases · We rarely think of a mixture of two gases as a solution; yet it conforms to our definition. Save when obvious chemical action occurs, gases mix in every proportion and apparently have no effect upon one another. When dealing with a solution of gases, we may assign to each *its fraction of the total pressure*, which will be the same as though the other gases were to be removed, leaving the one alone in the enclosing volume (Dalton's law, p. 71). Since there is practically no expansion or contraction when gases are mixed, the density of the mixture can be calculated from the known densities and percentages of the constituent gases.

Solutions of Gases in Liquids · While gases mix with each other in all proportions, a liquid will dissolve but a limited quantity of a gas; and when this limit is reached, the liquid is said to be *saturated*. Under these conditions the ratio of the quantity of the gas solute to the liquid solvent is called the *solubility* of the gas (under definite conditions of temperature and pressure). This may be expressed in a variety of ways, the most prevalent usage being to state the number of volumes of gas dissolved in one hundred volumes of the solvent.

SOLUBILITY OF GASES IN 100 ML OF WATER

NAME OF GAS	AMOUNT DISSOLVED AT 0° AND UNDER 760 MM PRESSURE	
	Grams	Milliliters
Ammonia	100.1192	129,890.00
Hydrogen chloride	82.9738	50,600.00
Sulfur dioxide	23.3513	7,979.00
Hydrogen sulfide	0.6726	437.00
Carbon dioxide	0.3386	171.30
Oxygen	0.0070	4.96
Nitrogen	0.0029	2.33
Hydrogen	0.0002	2.14

In respect to solubility, gases fall roughly into two classes: those of rather small solubility, such as oxygen, nitrogen, and hydrogen; and those of much larger solubility, such as ammonia, hydrogen chloride, and sulfur dioxide. In the case of the latter group there is always a change in the volume of the solvent when a large volume of gas is absorbed; the volume may increase markedly, as for solutions of ammonia in water. This volume change obeys no uniform laws, so that it is not possible to calculate the density of a solution, or from the measured density to infer the weight of gas dissolved. The slightly soluble gases do not cause any appreciable volume change in the solvent.

Factors Affecting the Solubility of Gases · The main factors affecting the solubility of gases are the specific properties of the solute and solvent, the pressure, and the temperature.

Effect of Specific Properties · As indicated above, different gases dissolve to different extents in water. Conversely, the same gas will dissolve to different extents in different liquids. These facts are the result of the specific properties of the gas and the liquid in which it dissolves.

The effect of these properties is particularly marked in the case of the very soluble gases, for which something akin to chemical reaction takes place when the gases dissolve, so that the solution of the gas acquires properties not shown by the solute or solvent alone. Thus, solutions of ammonia in water are basic in character, turning red litmus blue. Similarly solutions of sulfur dioxide and carbon dioxide are acidic. From any one of these solutions, however, the original gas may be removed; by raising the temperature, for example, ammonia, sulfur dioxide, and carbon dioxide are driven out of their solutions in water.

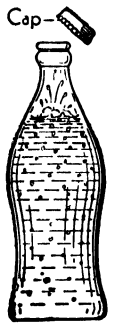


Fig. 12-1. Showing Escape of Carbon Dioxide When the Pressure of the Gas on a Solution Is Relieved by Removal of Cap

The explanation of the high solubility and the acquisition of new properties is that a chemical equilibrium exists in the solution, represented, for ammonia, by the equation

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

The double arrow indicates that the reaction is reversible and that it does not go to completion, so that all four constituents, ammonia, water, ammonium ion (NH_4^+), and hydroxyl ion (OH^-), are present in the solution at the same time.

Effect of Pressure · Gases are more soluble in liquids, the higher the pressure. A familiar example of this is furnished by a bottle of soda pop (Fig. 12-1). The gaseous solution is bottled under pressure; when the cap is removed, the carbon dioxide escapes because the pressure is lowered to atmospheric pressure.

Henry's Law · The change in solubility with change in pressure follows no standard rules for the more soluble gases. For the slightly soluble gases, however, like oxygen or hydrogen, *the weight of gas dissolved by a definite quantity of a given solvent is directly proportional to the pressure, provided the temperature remains constant* (Fig. 12-2). This statement is known as Henry's law, after the English chemist William Henry (1774–1836). Thus, if 1 g of a gas dissolves in 100 ml of water at atmospheric pressure, 2 g will dissolve under 2 atm at the same temperature. Under high pressures relatively large quantities of a gas dissolve; and when the pressure is diminished, a proportional weight of the gas escapes, as fine bubbles (*effervescence*).

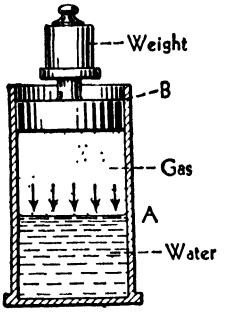


Fig. 12-2. A Gas Standing over Water in the Cylinder, A, Dissolves under the Pressure of a Weight Which Is Placed on the Tight-fitting Piston, B

When a mixture of two or more gases is maintained over a liquid, *each dissolves independently of the others and in accordance with its own partial pressure.* This is a necessary consequence of the law of Dalton (p. 71), which states that each gas in a mixture exerts its own partial pressure independently of the others. Each gas therefore dissolves independently of the others, in accordance with Henry's law.

Effect of Temperature · With rise in temperature, gases become less soluble, and, except in special cases in which constant-boiling solutions (p. 194) are formed, all of a dissolved gas can be driven out by boiling the solution.

While it is true that gases are more soluble in cold water than in warm water, they will not dissolve in ice. As water in tanks freezes from the outside inward, the dissolved air is liberated as bubbles, which are pushed ahead of the advancing front of ice crystals toward the interior (Fig. 12-3). For the same reason it is not wise to allow bottles of soda water or of other carbonated waters, placed, say, in the tray of an automatic refrigerator, to become cold enough to freeze the water. The considerable quantity of carbon dioxide gas thus liberated in the small free space of the bottle may develop sufficient pressure to cause a violent explosion. Such cases have been reported.

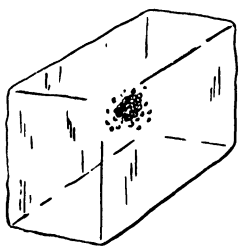


Fig. 12-3. Air Bubbles at the Center of a Cake of Ice

Solutions of Liquids in Liquids · Two liquids may conduct themselves toward each other in either of two ways: they may each reach a definite limit of saturation with the other, or they may be freely soluble (or

miscible) in all proportions. Several properties of liquid solutions are of importance.

1. **Vapor pressure.** Before mixing, each liquid has its own characteristic vapor pressure at the temperature in question. After mixing, it is found that each liquid has diminished the vapor pressure of the other, depending upon the relative amounts of the two liquids. The vapor pressure of the solution is never as great as the sum of the two original pressures; it may be greater or less than that of either liquid taken separately, or it may have an intermediate value. In any case the vapor from the solution at any definite temperature will be a mixture of that of each liquid, provided each has an appreciable vapor pressure.

2. **Boiling point.** On heating a solution of one liquid in another the total vapor pressure increases; and when it just exceeds the opposing pressure of the atmosphere, the solution boils. From what has been said in regard to the vapor pressure of solutions, it will be seen that we can form little idea as to the boiling point of a solution from the known boiling points of its constituents. It may be lower or higher than that of either constituent. Usually it has an intermediate value. Since the ratio by weight of the two vapors escaping from the solution is not in general the same as that of the two liquids constituting the solution, the composition of the liquid will change during the process of boiling. This will lead to variations in the composition of the vapor and a steady change in boiling point. It is only under exceptional conditions that a solution has a constant boiling point (and a constant composition) during distillation.

3. **Fractional distillation.** In distilling a solution the component having the greater vapor pressure will in general pass away from the solution more rapidly than the one of lower vapor pressure (higher boiling point). If the vapors are condensed, as described in the distillation of water, and the resulting liquid is collected in successive portions by changing the receiver at intervals, the first portions will be richer in the more volatile constituent, and the higher-boiling liquid will be largely obtained in the later portions. By repeating the process with each portion obtained in the first operation the two liquids may in time be separated from each other. Such a process is called *fractional distillation.* It is of the greatest importance in many industries, such as the refining of petroleum and the manufacture of alcohol and glycerin. We have already seen that nearly pure oxygen is prepared from liquid air by this process (p. 49).

4. **Constant-boiling solutions.** It occasionally happens that there is one particular concentration of a solution which has a lower vapor pressure (higher boiling point) than any other concentration or than that of either constituent taken separately. When such a solution is distilled,

one or the other constituent vaporizes more readily, and the concentration tends toward that of lowest vapor pressure. When this concentration is reached, the solution boils with constant boiling point like a pure substance, and the distillate has the same composition as the solution remaining in the still. Such a constant-boiling solution cannot be altered in composition by repeated distillation (under a given pressure). An example of such conduct is found in aqueous solutions of nitric acid, the constant-boiling solution consisting of 68 per cent acid and 32 per cent water. The constant-boiling solution of sulfuric acid contains 98.33 per cent acid, while that of hydrochloric acid contains 20.24 per cent acid, provided the pressure is standard (760 mm).

Constant-boiling solutions of maximum vapor pressure and minimum boiling point are also known. Ethyl alcohol forms a constant-boiling solution with water, which has a lower boiling point than either liquid.

Sparingly miscible liquids. If water is shaken for a few moments with ether or chloroform in a bottle and set aside for a short time, the more or less turbid liquid gradually clears and two liquid layers form, with the one of smaller density floating on the heavier. Each of these layers is a saturated solution. In the case of ether and water the upper layer consists of ether saturated with water; the lower, of water saturated with ether.

Solutions of Solids in Liquids · A solid dissolved in a liquid is by far the most familiar type of solution. In the following paragraphs it should be remembered that we are dealing with true solutions only. Thus, it is sometimes said that zinc dissolves in hydrochloric acid. In this case, however, the solution is preceded by a chemical reaction whereby the zinc is converted into zinc chloride, and it is this compound which is obtained when the solution is evaporated. With solutions such as we are now considering, evaporation leaves the solute in its original chemical condition.

Equilibrium in Saturated Solutions · When a lump of sugar is placed in a small beaker and covered with water, as represented in Fig. 12-4, it gradually diminishes in size and passes into solution; that is, particles leave it to wander through the solvent. If there is enough sugar, and if a long enough time elapses, the concentration of the sugar in the solution reaches *a definite limiting value*; and we say that the solution is *saturated.* Action, however, does not cease when the saturation point is reached. Molecules of the sugar continue to leave the lump and pass into the solution, while other molecules of sugar, previously dissolved, return to the lump from the solution. The rate of these two processes is exactly equal at saturation, so that the number of molecules of solute

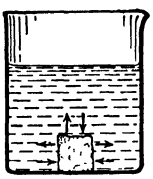


Fig. 12-4. Diagram Illustrating the Equilibrium of a Saturated Solution

leaving the solid and entering the solution in unit time is equal to the number of solute molecules leaving the solution and crystallizing out on the solid in the same unit of time. This is, then, another example of an equilibrium process (p. 170); and a *saturated* solution may be defined as one in which the dissolved solute is in *equilibrium with the undissolved solute.* The amount of solute present in a given quantity of solvent, when the solution is saturated, is called its *solubility.*

We know that molecules are still dissolving and crystallizing out after saturation is reached because if we make a saturated solution, using the "tagged" atoms of a radioactive substance, and then drop in a crystal of the same material which does not contain any radioactive atoms, we soon find that the nonradioactive crystal has acquired some radioactive atoms from the solution, having traded some of its ordinary molecules for some dissolved molecules containing radioactive atoms.

Rate of solution. Unless a solution is constantly stirred, it takes a long time to bring about saturation. The portion of the liquid in immediate contact with the solid dissolves it rapidly at first, then more and more slowly as saturation is approached. Meanwhile the dissolved molecules make their way, or *diffuse,* very slowly into the portions of the solvent not in contact with the solid. Thus, if some crystals of a highly colored substance, such as potassium permanganate, are placed in the bottom of a tall vessel full of water, it will take weeks or even months for the solution to become uniformly colored. Vigorous stirring rapidly brings all the solvent into contact with the solid, and approximate saturation is reached in a few minutes; but even then *complete* equilibrium is reached slowly at constant temperature.

Effect of Temperature on Solubility · Change of temperature always changes the solubility of a solute. As a rule, solids are more soluble in hot than in cold solvents, though occasionally the reverse is true. Many compounds of calcium, including the hydroxide, $Ca(OH)_2$, are of the latter class, while the solubility of common salt is very little affected by the temperature. Fig. 12-5 shows the change in solubility in a few familiar cases.

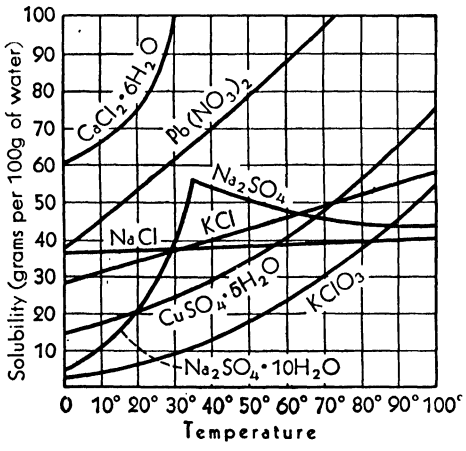


Fig. 12-5. Solubility Curves of a Few Compounds

Heat of Solution · When any crystalline solid dissolves, there is always a change in the temperature of the solvent. As a rule, the temperature falls, indicating absorption of heat; and

this is always true if the solid is more soluble in the hot solvent than in the cold. In case the solid is more soluble in the cold solvent, heat is evolved by the act of solution. The heat evolved or absorbed by 1 g of the solid to form a dilute solution is called the *heat of solution.* This value multiplied by the molecular weight is the *molecular heat of solution.* Heat is also absorbed when a very concentrated solution is diluted, and this is called the *heat of dilution.*

Frequently the solid combines with the water to form a stable compound as it passes into solution. Such an action may evolve much heat and so conceal the cooling effect of solution. For example, when anhydrous calcium chloride dissolves, it combines with the water to form a hydrate, giving off heat, just as it forms the hydrate $CaCl_2 \cdot 6\ H_2O$, when it is used in the drying of gases (pp. 93–94, 116).

Supersaturated Solutions, a Nonequilibrium Condition · The effect of changing temperatures on the solubility suggests a quicker way of making a saturated solution than that of simply stirring at constant temperature. Since the solubility of most solids increases with increasing temperature, we may approximately saturate a solution at a high temperature and then reduce the temperature to the desired point, *taking care to have some of the solid present all the time.* The excess of solute will crystallize out as the temperature is lowered, and almost at once the solution will come to the same saturation equilibrium as would be reached by the slower way of stirring at the desired temperature.

If we neglect to have some of the solid present while a concentrated solution cools, it may happen that the excess of solute will fail to crystallize out. The solution will then contain *more than the normal saturation quantity of the solute,* and is said to be *supersaturated.* This is apt to occur in the case of very soluble solids, with salts containing much water of hydration for example, with sodium sulfate ($Na_2SO_4 \cdot 10\ H_2O$), sodium thiosulfate ($Na_2S_2O_3 \cdot 5\ H_2O$), and ferric nitrate ($Fe(NO_3)_3 \cdot 6\ H_2O$) — and, in general, in all cases where the solution becomes notably viscous. It must be remembered that saturation is an *equilibrium*; and when one member of the equilibrium is absent, abnormal results may be expected. The introduction of even the smallest fragment of the solid solute into a supersaturated solution will bring about the crystallization of the excess of solute, and thus restore the saturation equilibrium appropriate to the lowered temperature.

Breaks in Solubility Curves · The solubility curve for $Na_2SO_4 \cdot 10\ H_2O$ (sodium sulfate) presents a singular feature (Fig. 12-5). Up to 32.4° it rises rapidly in a normal way, but above that point it steadily falls. An examination of the solids separating above and below this point shows that they are not the same. Below 32.4° the solid is $Na_2SO_4 \cdot 10\ H_2O$, while above this point it is the anhy-

drous salt Na_2SO_4. The point 32.4°, therefore, marks the temperature at which one salt changes into the other; like the freezing point of a liquid, it is called a *transition point.* Sharp breaks like this in a solubility curve always suggest some chemical transformation in the solute, so that the study of such curves is of great importance in giving information as to the changes taking place during a process of solution.

Concentration · The term *concentration* is much used by chemists, and its meaning is a very significant one. The term denotes *the quantity of solute dissolved in a given quantity of solvent or of solution.* The concentration of a solution may be expressed in a number of ways. Sometimes it is stated on a percentage basis. More often it is desirable to state the number of *moles* which a given volume of the solution contains. *When one mole (one gram-molecular weight or one gram-formula weight) is dissolved so as to make a liter of solution, the product is said to be a molar solution.* Thus, a molar solution of sodium hydroxide (NaOH) contains 40.005 g of the compound in 1 liter, while that of nitric acid (HNO_3) contains 63.016 g. If 15 g of sodium hydroxide is dissolved so as to form 1 liter of solution, the concentration is 0.375 molar (15 ÷ 40.005).

For some purposes it is more convenient to use *molal* solutions, which contain one gram-formula weight in 1000 g of solvent, or *normal* solutions. (Normal solutions will be defined in Chapter 14.) In addition, we use the relative terms *dilute* and *concentrated* for solutions of low and high concentrations respectively.

Concentration Is Independent of Quantity of Solution · If the molar solution made up, as in Fig. 12-6, is a solution of sugar, then 1 liter of solution contains 6.02×10^{23} sugar molecules; and 1 ml contains 6.02×10^{20} sugar molecules. Yet the two quantities of the solution have the same concentration. For, while 1 ml contains only $\frac{1}{1000}$ as many solute molecules, its volume is only $\frac{1}{1000}$ as great as the liter. The degree of "crowdedness" is the same in both. By dipping up or pouring out the proper number of milliliters of a molar solution, one can measure out a required number of molecules or ions, or measure out a known fraction of a mole.

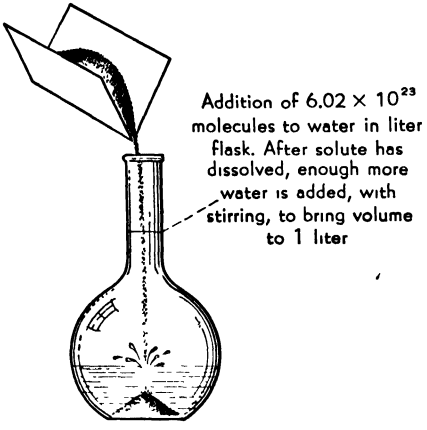


Fig. 12-6. Preparation of a Molar Solution

Solutions of Solids in Solids · A number of cases have been noted in which one solid slowly diffuses into another. Gold will diffuse into lead,

and lead into gold, when clean pieces of the two metals are tightly clamped together; copper-plated zinc gradually turns lighter in color from mutual diffusion of the two metals. The products in such cases are called *solid solutions*. Similar solutions can be prepared in special cases by melting the two solids together. If they form a liquid solution, they may also freeze as a homogeneous solid with the properties of a true solution (Fig. 12-7). (In other cases solid solutions are not formed; one solid or the other separates as a pure material, or definite compounds form.)

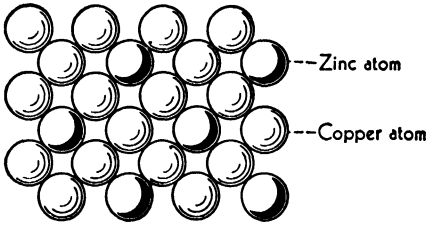
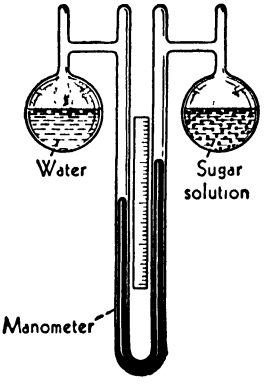


Fig. 12-7. Ordinary Brass Is a Solid Solution of Copper and Zinc Mixed in the Ratio of About 3 Atoms of Copper to 1 Atom of Zinc

Properties of a Solvent Modified by a Solute · The properties which a solvent (such as water) possesses when pure are often greatly modified when a solid is dissolved in it. Among these properties are (1) *vapor pressure*, (2) *boiling point*, (3) *freezing point*. These effects are not only interesting and important in themselves, but on them are based methods for finding the molecular weights of solutes. In the present treatment we shall deal only with covalent solutes, which *do not furnish ions*; in the next chapter solutions containing ions will be considered.

1. **Lowering of the vapor pressure.** A solution of a solid in a liquid has a lower vapor pressure than that of the liquid itself. This can be easily shown, with a manometer, for solutions of sugar in water (Fig. 12-8). No completely satisfying explanation for the lowering is known. Perhaps the sugar molecules act as a "screen" and interfere with the escape of solvent molecules, and so lower the vapor pressure.



F.g. 12-8. The Air Is Pumped Out of the Apparatus. Then the Difference in Levels of the Mercury Columns Gives the Difference in Pressure between the Water and the Solution

After many years of careful experimental work, the French scientist Raoult found (1) *that the lowering of vapor pressure at a given temperature is directly proportional to the molal concentration of the solution*, and (2) *that the effect is the same for all solutes, regardless of their chemical nature, provided that they do not have an appreciable vapor pressure of their own and do not furnish ions in solution.* In other words, at a given temperature the lowering of the vapor pressure of a given solvent depends *only on the number* of solute molecules

in a given quantity of the solvent. Raoult's law holds true only for dilute solutions.

Deliquescence · When exposed to moist air, many solids absorb water to such an extent that they gradually pass into solution. This spontaneous process is called *deliquescence*, and the solid is said to be *deliquescent*. The explanation of this process is as follows:

Apparently all solids tend to condense a film of moisture on their surface, and the film soon becomes a saturated solution by dissolving the solid. *If the solid is very soluble*, the solution so formed will be very concentrated, and its vapor pressure very small. If the vapor pressure of the solution should be smaller than the average value for the partial pressure of the water vapor normally present in air (which may be taken as about 12 mm at ordinary temperatures), then this solution cannot possibly evaporate. On the contrary, it will absorb moisture from the air. This will dilute the solution, which will then dissolve more of the solid, and the process will continue until all the salt has dissolved. To say that a salt is deliquescent, in a climate of average moisture, is really to imply that it is very soluble.

2. Elevation of the boiling point. Since the boiling point of a liquid is the temperature at which its vapor pressure just exceeds the opposing pressure of the atmosphere, it is evident that any condition which *lowers the vapor pressure will raise the boiling point*, since the liquid will have to be heated to a higher temperature to regain its original vapor pressure. This is shown schematically in Fig. 12-9, which represents the vapor pressure–temperature curve for a pure liquid, as in Fig. 11-13, together with the corresponding curve for a solution of a definite concentration. In the course of his experiments, Raoult found that *the elevation of the boiling point*, like the lowering of the vapor pressure, *is proportional to the molal concentration of the solution.*

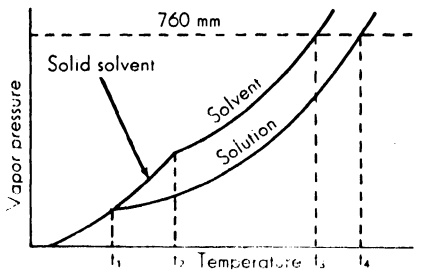


Fig. 12-9. Showing that a Solution Has a Lower Vapor Pressure than the Solvent

Also, at t_4, the boiling point of the solution is greater than at t_3, and at t_1 the freezing point of the solution is less than that of the solvent at t_2

It follows that gram-molecular weights of any substances not electrovalent and not having a vapor pressure of their own, when dissolved in a definite weight of a solvent, produce the same rise in the boiling point. But the rise is different for different solvents. The boiling-point elevation produced by 1 g-mol. wt of solute added to 1000 g of water

(a molal solution, p. 198) is 0.518°. Since the boiling-point elevation is proportional to the concentration, the boiling point of a 0.5 molal solution will be $0.5 \times 0.518 = 0.259°$ higher than that of pure water.

The fact that the boiling point of a solution is higher than that of the pure solvent is qualitatively familiar in the process of candymaking, where water is boiled off from a concentrated sugar solution; the concentration is thus further increased, with a consequent rise in the boiling point. In this case the concentration of the solution is estimated roughly from the boiling point as measured on a candy thermometer; when the boiling temperature reaches 238° F, for example, the solution is concentrated enough so that, on cooling to crystallize, the candy will be of puttylike, "soft ball" consistency.

3. **Lowering of the freezing point of the solvent.** When an unsaturated solution is cooled sufficiently, it does not freeze *as a solution*, but crystals of the *pure solvent* are formed. Since at the freezing point the vapor pressures of solid and liquid are equal, and since the vapor pressure of the solution is less than that of the pure solvent, it is evident, as shown in Fig. 12-9, that the freezing point of the solution is below that of the pure solvent. Doubtless one of the first observations of this kind was that salt water remains unfrozen while fresh water close by freezes. It is to lower the freezing point of water that we add various compounds (sometimes sugar, but usually alcohol, glycerin, or ethylene glycol) to the water in an automobile radiator in cold weather.

Raoult found that *the freezing-point depression also was proportional to the molal concentration of the solution*, and was the same for covalent solutes in the same solvent, as shown for water in the table below. Thus, a gram-molecular weight of solute dissolved in 1000 g of water lowers the freezing point approximately 1.86° (called the freezing-point constant for water).

LOWERING OF THE FREEZING POINT OF WATER

SOLUTE	FORMULA	LOWERING PRODUCED IN 1000 G OF WATER BY 1 G-MOL. WT OF SOLUTE
Methyl alcohol (methanol)	CH_4O	1.86°
Ethyl alcohol	C_2H_6O	1.83°
Dextrose	$C_6H_{12}O_6$	1.92°
Glycerin	$C_3H_5(OH)_3$	1.92°
Urea	$CO(NH_2)_2$	1.86°

Every *solvent* has its own characteristic freezing-point constant; thus for acetic acid it is 3.9°, for benzene 5.1°, for naphthalene 6.8°.

Molecular-Weight Determination · Since the vapor-pressure lowering, boiling-point elevation, and freezing-point depression are each propor-

tional to the molal concentration of a solution, that is, to the *number* of solute molecules in a solution, it is possible to determine the molecular weight of a dissolved compound from measurements on one of the above-mentioned properties—for example, the freezing-point depression.

Example. On a sensitive thermometer the freezing point of water was found to be exactly 0°, while a solution of 0.775 g of ethylene glycol, dissolved in 25.0 g of water, froze at − 0.93°. Since the freezing-point depression is proportional to the molal concentration, the molal concentration is evidently $\frac{0.93}{1.86} = 0.5$ molal. The weight of ethylene glycol in 1000 g of water would be $\frac{0.775}{x} = \frac{25}{1000}$, whence $x = \frac{1000 \times 0.775}{25} = 31.0$ g. But this is a 0.5 molal solution; so a 1 molal solution would contain $2 \times 31.0 = 62$ g of ethylene glycol in 1000 g of water, and the molecular weight of ethylene glycol is 62. The molecular weight obtained in this way is likely to be only approximate.

Lowest Freezing Point of Solutions · If we cool a *dilute* solution, crystals of the solvent are formed; and if we continue the cooling, the solution grows more and more concentrated, owing to the removal of the solvent as crystals. Finally it becomes *saturated*, and then crystals of *both solvent and solute* are formed. The temperature at which this happens is the lowest freezing point of the solution. The resulting solid, consisting of two kinds of crystals in fixed proportion, is called a *eutectic*; and the temperature at which the eutectic freezes is called the *eutectic temperature*.

Freezing mixtures. It is a familiar fact that when we put ice into water at room temperature, the temperature of the mixture falls to the freezing point of water because of the absorption of heat by the melting of the ice. In like manner, if we mix ice, water, and a soluble solid, the temperature will fall to the eutectic temperature, provided there is enough ice and solid solute present (and if the mixture is well insulated). The absorption of heat is due to both the melting of ice and the dissolving of the solid solute. The more soluble the solute, the lower the eutectic temperature. We often make use of a mixture of crushed ice and solid salt as a freezing mixture to secure temperatures somewhat below 0°. The eutectic temperatures (sometimes called cryohydric temperatures when *water* is the solvent) of a few salt mixtures are shown in the following table:

EUTECTIC (OR CRYOHYDRIC) TEMPERATURES OF ICE AND VARIOUS SALTS

SALT	TEMPERATURE	SALT	TEMPERATURE
Potassium nitrate . . .	− 3°	Sodium nitrate	− 18.5°
Sodium thiosulfate . . .	− 11°	Sodium chloride	− 22.4°
Ammonium chloride . .	− 15.8°	Calcium chloride . . .	− 54.9°
Ammonium nitrate . . .	− 17.5°	Hydrogen chloride . . .	− 86.0°

Osmosis · Closely related to the lowering of the vapor pressure, to the elevation of the boiling point, and to the depression of the freezing point is the phenomenon of *osmosis*. This is the passage of a solvent from a dilute solution (or from a pure solvent) through a membrane into a more concentrated solution.

The membrane must be semipermeable, that is, such that it will allow molecules of solvent to pass through readily, but will not allow molecules of solute to pass. A piece of parchment paper or nonwaterproof cellophane is semipermeable in this sense, and may be used to demonstrate osmosis. The membrane is fastened tightly over the bell of a thistle tube with cord and sealing wax (Fig. 12-10). A sugar solution is placed in the vessel so constructed, which is then immersed in pure water. Osmosis starts, and the volume of the sugar solution slowly increases as the water enters through the membrane.

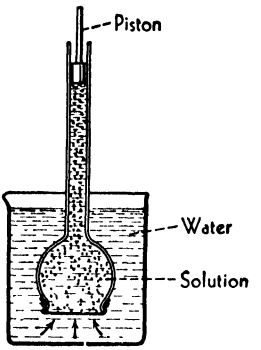


Fig. 12-10. Diagram Illustrating Meaning of Osmotic Pressure

Osmotic Pressure · If we could fit the tube in Fig. 12-10 with a piston, as shown, and with it apply a sufficiently large pressure on the solution, osmosis would stop. In fact, by pushing hard enough on the piston, water could be squeezed out of the solution, through the membrane, back into the outer vessel.

That pressure which, when applied to a solution, will just prevent the entrance of solvent into it through a semipermeable membrane is the osmotic pressure of the solution. The pressure need not be applied with a piston. The hydrostatic pressure of a long vertical column of the solution may serve the same purpose.

Quantitative Measurements · It would not be possible to measure the osmotic pressure in the apparatus of Fig. 12-10, because, unless the solution were extremely dilute, the membrane would break before the pressure on the piston reached the osmotic pressure. For quantitative measurements the membrane must be supported in some way, such as by precipitating it as a film in the pores of an unglazed porcelain wall.

Isotonic Solutions · Something similar to the breaking of the parchment membrane, due to the osmotic pressure, occurs if a blood corpuscle is placed in pure water. The liquid inside the corpuscle contains dissolved substances, and water enters from the outside by osmosis through the membrane covering the corpuscle. This causes the corpuscle to swell and finally to burst. To avoid this or similar osmotic effects in medical practice, injections into the body are always made with *isotonic solutions*,

in which the concentration is so fixed that these solutions will have the same osmotic pressure as the body fluids.

The Laws of Osmotic Pressure · The results of extensive experimental study of osmotic pressure show that for covalent compounds it (1) is approximately proportional to molal concentration, (2) is independent of the nature of the solute particles, and (3) is proportional to the absolute temperature. Such behavior recalls the gas laws. Indeed, it has been found to be true that the *osmotic pressure of a solution is approximately equal to the gas pressure which the solute would exert if it were a gas occupying the same volume as the solvent, at the same temperature.*

For instance, 1 g-mol. wt of a gas, in 22.4 liters at 0°, exerts a pressure of 1 atm. At 20° the pressure is $\frac{293}{273} \times 1$ atm = 1.07 atm. Similarly 1 g-mol. wt of sugar dissolved in 22.4 liters of water, at 20°, has an osmotic pressure of about 1.07 atm.

QUESTIONS

1. Distinguish between (*a*) molar and molal concentrations; (*b*) homogeneous and heterogeneous mixtures; (*c*) compound and mixture; (*d*) mixture and solution; (*e*) compound and solution.

2. (*a*) State Henry's law. (*b*) The gases carbon dioxide and sulfur dioxide do not follow Henry's law. Why not?

3. (*a*) State Raoult's law. (*b*) Explain deliquescence. (*c*) Show how, on the basis of Raoult's law, molecular weights of certain solutes could be determined. (*d*) The molecular weights of certain types of solutes could not be so determined. What are the types?

4. (*a*) Indicate, with a graph, the type of vapor pressure-temperature diagram which a pure solvent and a solution will have, and show on the graph what happens to the freezing point and boiling point of the solvent when the solute is added. (*b*) Define the boiling point and freezing point in terms of vapor pressure.

5. In three separate beakers are placed (*a*) a dilute solution of sodium thiosulfate, (*b*) a saturated solution of sodium thiosulfate, and (*c*) a supersaturated solution of sodium thiosulfate. A crystal of solid sodium thiosulfate is added to each beaker. What change will take place in the concentration of sodium thiosulfate in solution in each case?

6. A beaker, *X*, was filled two-thirds full with a concentrated solution of sugar in water, and another beaker, *Y*, was filled two-thirds full with water. The two beakers were then covered with a bell jar and allowed to stand. After some time beaker *X* was found to be full to overflowing, while the level of water in beaker *Y* had lowered appreciably. How do you account for this result?

7. Explain why the temperature drops below 0° when ice, water, and sugar, all at 0°, are mixed together.

8. Describe an experiment to prove that a kinetic equilibrium is established in a saturated solution between the dissolved solute and the undissolved material.

9. Why does a brick of ice cream melt when placed in a refrigerator at 0°?

10. Henry's law may be stated also in terms of the volume of a gas dissolved, thus: "The volume of a gas dissolved in a liquid is *independent* of the pressure." How do you reconcile this with Henry's law as usually stated?

11. What is the solubility of each of the following compounds in water at the temperature designated: (*a*) lead nitrate at 50°; (*b*) sodium chloride at 70°; (*c*) copper sulfate at 40°?

12. Do you know (*a*) of any gas that is more soluble in hot water than in cold; (*b*) of any solid that is more soluble in cold water than in hot?

13. How could you separate (*a*) a gas from a liquid in which it is dissolved; (*b*) a liquid from a liquid in which it is dissolved; (*c*) a solid from a liquid in which it is dissolved?

14. Suppose you were given the problem of finding some liquid that could be safely and economically used in the radiator of an automobile in cold weather. What properties should such a liquid have?

15. The compound ammonium chloride (NH_4Cl) dissolves in water, with the absorption of heat. Predict, on the basis of Le Châtelier's principle, whether the solubility of ammonium chloride is greater in hot water or in cold.

PROBLEMS

1. Calculate the number of grams of each of the following compounds that will be required to prepare 1 liter of a molar solution: (*a*) potassium nitrate (KNO_3); (*b*) potassium chlorate ($KClO_3$); (*c*) sugar ($C_{12}H_{22}O_{11}$).

2. Which of the following solutions will have the lower freezing point: (*a*) 100 g of sugar ($C_{12}H_{22}O_{11}$) dissolved in 1 liter of water or (*b*) 100 g of alcohol (C_2H_6O) dissolved in 1 liter of water?

3. Other things being equal, which produces the lower freezing point when added to 10 liters of water in the radiator of an automobile, 10 lb of pure alcohol (C_2H_6O) or 10 lb of glycol ($C_2H_6O_2$)?

4. One hundred milliliters of water dissolves 4.96 ml of oxygen under standard conditions; an equal volume of water dissolves 2.33 ml of nitrogen under the same conditions. Suppose that air were enclosed over 100 ml of water under standard conditions. (*a*) Calculate the number of milliliters of oxygen and of nitrogen that would be dissolved. (*b*) How would the ratio of free oxygen to nitrogen in the dissolved gases compare with their ratio in the air?

5. A solution of 2.8 g of urea in 80 g of water was found to raise the boiling point 0.302°. What is the molecular weight of urea?

6. Calculate the molar concentration of a solution of sulfuric acid which was found to contain 8.8 g of sulfuric acid in 220 ml of solution.

7. What weight, in grams, of a hydrochloric acid solution containing 36 per cent of HCl is required to make a liter of 1 molar hydrochloric acid solution?

8. What osmotic pressure would be developed by a solution of 4.4 g of dioxane (formula, $C_4H_8O_2$) dissolved in 280 ml of water at 15°?

CHAPTER 13

IONIZATION; ELECTROCHEMISTRY

Ionization

In Chapter 12 it was shown that the introduction of a solute into a solvent changes the vapor pressure, freezing point, and boiling point of the solvent, and gives rise to an osmotic pressure. It was also shown that these effects are dependent on the *number* of molecules of solute and not on the *kind* of molecules in a given weight of solvent. The regularities of these effects were summarized in laws, and were made the basis of methods for determining the molecular weights of compounds.

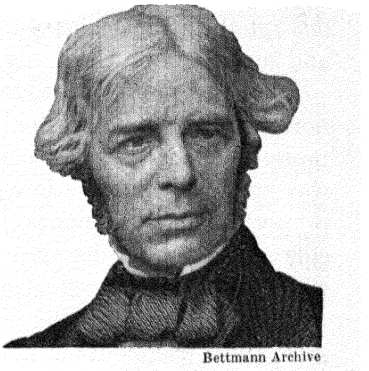
Irregularities in the Effects Produced by Solutes · Experiments have shown that compounds can be divided into two classes on the basis of the effects they produce on the properties of a solvent: (1) those which give the normal molecular effect, just indicated, on freezing point, vapor pressure, boiling point, and osmotic pressure, and (2) those which produce excessive effects on these properties. This distinction may be seen by considering the lowering of the freezing point:

FREEZING-POINT LOWERING PRODUCED BY SEVERAL KINDS OF SOLUTES

SUBSTANCE	FORMULA	LOWERING OF FREEZING POINT PRODUCED BY DISSOLVING 1 G FORMULA WT IN 1000 G OF WATER
Dextrose	$C_6H_{12}O_6$	1.92°
Alcohol	C_2H_5OH	1.83°
Urea	$CO(NH_2)_2$	1.86°
Sodium hydroxide	NaOH	3.44°
Sodium chloride	NaCl	3.37°
Sodium nitrate	$NaNO_3$	3.02°
Hydrogen sulfate	H_2SO_4	4.04°
Calcium nitrate	$Ca(NO_3)_2$	4.59°
Magnesium sulfate	$MgSO_4$	2.02°

The substances in the second group are said to have *abnormal* freezing-point depressions. Experiments show that solutions of these compounds show similar abnormal boiling-point elevations and abnormal osmotic pressures.

Electrolytes · The Swedish chemist Arrhenius (Fig. 13-2) was struck by the fact that the compounds which showed these abnormal effects be-



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Fig 13-1. Michael Faraday (1791–1867) Pupil of Sir Humphry Davy, and his successor as director of the laboratories of the Royal Institution. One of the world's greatest experimental philosophers both in chemistry and in physics. A pioneer in the liquefaction of gases. The discoverer of benzene, and of the fundamental principles of electrical induction, upon which all electric motors and dynamos depend. He first demonstrated a connection between magnetism and light.

longed to that group of compounds which Faraday (Fig. 13-1) had long before named electrolytes. In his experiments on electricity Faraday had observed that while pure water was a very poor conductor of electricity, the solution of certain substances in water made it a good conductor. He called these substances *electrolytes*, distinguishing them from the nonelectrolytes, whose water solutions conducted the electric current no better than water itself.

Faraday's Ions · In order to explain the conduction of electricity through a solution, Faraday reasoned that charged particles were present in the solution, and that these particles, loaded with very small but definite quantities of electricity, moved through the solution to the electrodes. Solutions of nonelectrolytes, on the other hand, for some reason did not contain charged particles, and hence their solutions were nonconductors. He called the charged particles formed in electrolyte solu-



Fig. 13-2. Svante August Arrhenius (1859–1927) Distinguished Swedish chemist, director of the Nobel Institute of the Academy of Sciences, Stockholm. He made many important discoveries concerning the relation between electrolytic phenomena and the physical and chemical properties of compounds. Known chiefly as the founder of the theory of electrolytic dissociation, or ionization. Recipient of the Nobel prize for chemistry in 1903.

tions *ions* ("goers"), but never very clearly pictured what they are or how they are formed.

It came to be believed (*erroneously*, as it turned out) that the current disrupted the molecules of the electrolyte, loaded the ions with electricity, and sent them on their way.

The Theory of Ionization · Arrhenius, in 1887, suggested that the abnormal effects observed for solutions of electrolytes were the result of the presence of charged particles in the solution *even before* the electric current was applied. Raoult's law showed that the freezing-point lowering was proportional to the concentration of dissolved molecules; if each molecule separated, on dissolving, into two or more smaller particles, each of which had the same effect on the freezing-point depression as that of the whole molecule, then the observed abnormal effect would appear. If, in turn, these fragments of molecules carried electric charges, then the ions, which had been postulated by Faraday, would also be accounted for.

The assumption that dissociation into charged particles occurred was necessary on chemical grounds, as well as to explain the behavior of Faraday's electrolytes. A compound like sodium chloride, for example, could not separate into sodium and chlorine *atoms* in water solution, since sodium reacts with water to produce hydrogen, and no hydrogen is evolved when sodium chloride dissolves in water. If it separated into the charged ions Na^+ and Cl^-, however, these would not be expected to show the properties of the uncharged atoms. An ion, in other words, is something different from an atom, a fact which is indicated in the formula of an ion by including the charge as an integral part of the formula, as for the sodium and chlorine ions above.

Ions · Not all electrolytes form ions from single atoms. Solutions of sulfuric acid, for example, contain sulfate ions of the formula SO_4^{--}, a radical with an electric charge. This ion is relatively stable, and in the ordinary reactions of sulfuric acid it remains as a unit of five atoms with two negative charges. An *ion* may be defined, then, as *an atom or radical carrying an electric charge*. The sign and magnitude of the charge on an ion are the same as the electrovalence of the element or radical, as shown for a few examples below.

ELEMENT OR RADICAL	ELECTROVALENCE	ION
Sodium	+1	Na^+
Chlorine	−1	Cl^-
Magnesium	+2	Mg^{++}
Sulfate	−2	SO_4^{--}
Oxygen	−2	O^{--}

In any compound the total positive charge must equal the total negative charge, since the compound as a whole is electrically neutral; thus, if the sodium ion is Na^+, the chlorine ion in NaCl must be Cl^- in order that sodium chloride may be neutral. Note that this does not require that there be the same number of positive ions as negative ions, since the magnitude of the charge on the two kinds of ions may be different, as in $CaCl_2$ (Ca^{++}, 2 Cl^-).

Formation of Ions · How does a sodium atom become positively charged, forming a sodium ion? Evidently (p. 40) it does so by the loss of an electron from the outer shell of the neutral atom, which leaves one less electron in the shells of the atom than the number of positive charges on the nucleus. Thus, we may write the formation of the sodium ion as follows:

$$Na \longrightarrow Na^+ + e^- \qquad (1)$$

Similarly the chloride ion is formed from the chlorine atom by the gain of an electron, which gives one more electron than can be neutralized by the positive charge on the chlorine nucleus:

$$Cl + e^- \longrightarrow Cl^- \qquad (2)$$

Ions, then, are formed from atoms by the gain or loss of one or more electrons. Conversely, atoms may be formed from ions by the loss or gain of one or more electrons. This is equivalent to the reversal of the reactions represented in equations (1) and (2).

It should be noted that in chemical reactions electrons are not observably products and reactants, as equations (1) and (2) imply. Free electrons exist in detectable concentrations only in evacuated spaces, as in a radio vacuum tube.

Oxidation-Reduction Reactions · In chemical reactions, however, the electron given up by one atom in becoming a positive ion (equation (1)) is immediately taken up by another atom or radical, which thereby becomes more negative (equation (2)). Therefore the actual chemical reaction which would occur if chlorine gas were brought in contact with sodium consists in the transfer of an electron from the sodium atom to the chlorine atom:

$$2\ Na + Cl_2 \longrightarrow 2\ Na^+ + 2\ Cl^- \qquad (3)$$

In this electron-transfer reaction we say that the sodium has been oxidized, in agreement with the use of the term *oxidation* to describe what happens when sodium reacts with oxygen. Here, again, the sodium atoms lose electrons (and the oxygen atoms gain them):

$$4\ Na + O_2 \longrightarrow 4\ Na^+ + 2\ O^{--} \qquad (4)$$

Oxidation, then, is a *loss of electrons* from an atom or ion. The process of *gaining electrons* is called *reduction*, and we say that the chlorine atoms and the oxygen atoms in equations (3) and (4) are reduced. Since the electrons lost by one substance are gained by another, it is evident that oxidation and reduction cannot occur separately, and the electron-transfer reactions expressed by equations (3) and (4) are known as oxidation-reduction reactions.

It will be observed that in equations (3) and (4) the electrovalence has changed from 0 to + 1 in the case of sodium, from 0 to − 1 in the case of chlorine, and from 0 to − 2 in the case of oxygen. Oxidation and reduction may be expressed also in terms of valence, oxidation as an increase in positive valence or a decrease in negative valence, and reduction as a decrease in positive valence or an increase in negative valence (see pages 42, 254).

Ionic Crystals · The result of the electron-transfer reaction of equation (3) is that the compound sodium chloride is formed. This exists at ordinary temperatures as a crystalline solid, in which sodium and chloride ions are arranged in a definite pattern (Fig. 11-28, p. 187). When sodium chloride crystals are dissolved in water, the electrostatic forces between the oppositely charged ions are weakened, so that the ions separate from each other. Each ion then behaves like a separate molecule as far as Raoult's law is concerned, which results in the abnormal effects previously noted.

Ions from Covalent Molecules · Solutions containing ions are sometimes formed when covalent molecules are dissolved in water. For example, when ammonia dissolves, reaction takes place, with the formation of ions (p. 192):

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \qquad (5)$$

Further, when the covalent gas hydrogen chloride dissolves in water, hydrogen and chlorine ions are formed as a result of reaction with the water. In the case of hydrogen chloride this reaction is nearly complete, so that the solution contains practically no hydrogen chloride molecules; with ammonia or acetic acid (p. 212) the reaction is incomplete, and most of the solute remains as molecules rather than as ions.

Interionic Attraction · The data in the table on page 206 show that the freezing-point depression produced by the electrolytes is not as great as that to be expected for complete separation of the ions. For sodium chloride, for example, the freezing-point depression for the molal solution is not quite twice that for a molal solution of a nonelectrolyte, as would be expected if two ions were formed for each molecule. Similarly the freezing-point depression for calcium nitrate is not that to be expected for three ions from each molecule, and for magnesium sulfate the effect

is only slightly greater than for a nonelectrolyte. The reason for this is that the electrostatic forces between the ions are not obliterated completely in the solution, but are still sufficiently powerful to pull the ions toward one another. As a result of this interionic attraction, the ions are not completely freed from one another, and the partial effects recorded in the table are observed experimentally. Similar partial effects are observed for vapor-pressure lowering, boiling-point elevation, and osmotic pressure.

1. **Effect of charge.** As one would suppose, the electrostatic forces are greater, the higher the charge on the ions. This explains the difference between sodium chloride, for example, and magnesium sulfate (see the table on page 206). The doubly charged magnesium (Mg^{++}) and sulfate (SO_4^{--}) ions have a greater attraction for each other than Na^+ and Cl^-, and consequently a smaller effect on the depression of the freezing point.

2. **Effect of solvent.** The magnitude of the attractive forces between ions depends upon the solvent in which they are dissolved, and is determined by the insulating properties of the solvent as expressed by a quantity called the dielectric constant. In water, with a high dielectric constant, the electrostatic forces are small, so that the ions are relatively free. Most other solvents have smaller dielectric constants than water, so that the electrostatic forces are greater, with consequent greater interionic attraction. Some solvents, like ether and benzene, have such low dielectric constants that the interionic attraction is so great that there is little or no separation of the ions of those few electrolytes which will dissolve in them.

3. **Effect of dilution.** Besides the dependence of the electrostatic forces on the charge of the ions and on the solvent, they depend also upon the distance between the ions, being smaller the farther apart the ions are. This may be observed experimentally. The effect of dilution on the freezing-point depression is shown in the table below, in which the

EFFECT OF DILUTION ON INTERIONIC ATTRACTION

1	2	3	4	5	6	7	8
CONCN. IN MOLES/ 1000 G H_2O	FREEZING-POINT DEPRESSION				RATIO		
	KCl	$C_{12}H_{22}O_{11}$ SUGAR	K_2SO_4	$HC_2H_3O_2$ ACETIC ACID	$\frac{KCl}{C_{12}H_{22}O_{11}}$	$\frac{K_2SO_4}{C_{12}H_{22}O_{11}}$	$\frac{HC_2H_3O_2}{C_{12}H_{22}O_{11}}$
0.1	0.345°	0.188°	0.432°	0.1897°	1.84	2.30	1.01
0.05	0.175°	0.0935°	0.228°	0.0960°	1.87	2.43	1.02
0.01	0.0361°	0.0186°	0.0501°	0.0196°	1.94	2.69	1.05
0.005	0.0182°	0.00930°	0.0258°	0.0099°	1.96	2.77	1.06
0.001	0.00366°	0.00186°	0.00528°	0.00205°	1.97	2.83	1.10

freezing-point depression for the electrolyte potassium chloride is compared with that for the nonelectrolyte sugar at various concentrations. The sixth column of the table shows that as the solution becomes more dilute, the ratio of the freezing-point lowering for the electrolyte to the freezing-point lowering for the nonelectrolyte approaches more and more closely to 2.0, the expected value for complete separation of the two ions in potassium chloride. Column 7 shows a similar effect for potassium sulfate, the value 3.0 being approached with increasing dilution.

Strong and Weak Electrolytes · If the data of Column 6 are compared with those of Column 8, which records data for acetic acid, it is seen that the ratio of the freezing-point depression for acetic acid to that for sugar is only slightly greater than 1.00 at concentrations where the corresponding ratio for potassium chloride is nearly 2.00. Comparison with results for other compounds indicates that there are many electrolytes which behave like potassium chloride, and many others which show the behavior of acetic acid. The difference between the two groups is so great that it is evident that they represent two different classes of compounds, and that the effects of dilution in the latter group cannot be due simply to the freeing of the ions from their interionic attraction. Rather, in this case, ions are actually formed from covalent molecules, in a reversible reaction:

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^- \qquad (6)$$

At ordinary concentrations the ionization is not very great, but it increases with dilution, owing to the lessened chance that the ions have of recombining, the farther apart they are.

Electrolytes which behave like potassium chloride are called *strong electrolytes*; this class includes most salts and strong acids and bases like hydrochloric acid and sodium hydroxide. Those of the acetic acid type are called *weak electrolytes*; ammonium hydroxide belongs to this class. The difference between the two classes is that strong electrolytes have only ions present in solution, held together to a greater or less extent by interionic attractive forces determined by the charge, the solvent, and the dilution. Weak electrolytes, on the other hand, exist in solution predominantly as covalent molecules, only a few of which are ionized at any one time. The ions thus formed have electrostatic forces existing between them, but the effects of dilution on these are largely masked by the effects produced by the change in the actual number of ions resulting from the ionization of a greater fraction of the covalent molecules as the dilution is increased. The difference between strong and weak electrolytes is experimentally more evident from a consideration of the conductivity of solutions containing electrolytes.

Electrolytic Conduction · If two oppositely charged electrodes are placed in a solution containing ions, the positive ions will be drawn toward the negative electrode, and the negative ions will be drawn toward the positive electrode. This movement of charged particles through the solution results in a transfer of electric charge; we recognize this as an electric current, and say that the solution conducts the electric current. This type of conduction, which results from the motion of ions through the solution, is called *ionic* or *electrolytic conduction* in order to distinguish it from *electronic* or *metallic conduction*, which occurs when a current of electrons flows through a wire.

The amount of charge transferred across the solution in unit time will depend upon the number of ions present in the solution and the speed with which they move. Large ions move more slowly than small ions, and doubly or triply charged ions are held back more by the interionic attraction than are singly charged ions. These are relatively small effects, however, compared with those resulting from the differences in the number of ions in solutions of strong and weak electrolytes. In the case of strong electrolytes, the dissolved substance is all in the form of ions, and the conductivity is high; in the case of weak electrolytes, mostly covalent molecules are present in the solution, with comparatively few ions, and the conductivity is low.

Illustrative experiment. The fact that solutions differ greatly in electrical conductance, even at equivalent concentrations, may be demonstrated with the apparatus represented in Fig. 13-3. Solutions of equivalent concentrations are placed successively in the bottle, *A*, and the wire electrodes are dipped into the solution. Connection with the lighting circuit is made by the cord and plug, *B*. If the solution is a good conductor, the current will flow through the lamp, *C*, which will then glow.

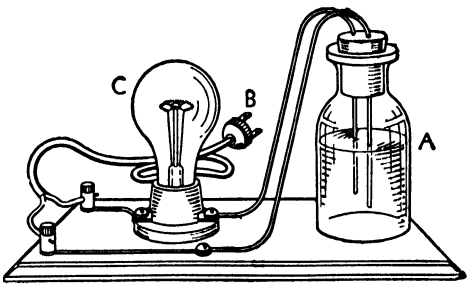


Fig. 13-3. Apparatus for Testing the Conductivity of a Solution

Electrolytic conduction can also occur if an ionic crystal is melted. The ions are released from the rigid-patterned arrangement of the crystal (p. 187) and are free to move; hence if electrodes are placed in the melt, the ions will move toward the electrode of opposite charge, and the melt will conduct a current.

Speed of Ionic Reactions · Reactions involving only electrolytes are much more rapid than most of those involving nonelectrolytes. For ex-

ample, if solutions of sodium chloride and silver nitrate (both electrolytes) are mixed at room temperature, a precipitate of silver chloride forms immediately. On the other hand, if silver nitrate solution is added to a nonelectrolyte containing chlorine, such as carbon tetrachloride, a precipitate forms only after heating for a long period of time. The reason for the behavior of the two electrolytes is that the formation of silver chloride consists solely in the combination of the silver ions and chloride ions *already present in the solutions* of silver nitrate and sodium chloride before mixing, so that the reaction is

$$Ag^+, NO_3^- + Na^+, Cl^- \longrightarrow AgCl\downarrow + Na^+, NO_3^- \qquad (7)$$

or simply

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow \qquad (8)$$

No chloride ions are present in the solution of the nonelectrolyte carbon tetrachloride, and no reaction with silver ions occurs, until hydrochloric acid has been formed by the slow chemical reaction of carbon tetrachloride with the water present.

Properties of Ionic Solutions Are Those of the Ions · It is evident also that all solutions containing the chloride ion will behave similarly toward the silver ion, since it makes no difference whether the chloride ion was originally paired with the sodium ion or potassium ion or hydrogen ion or any other. The essential reaction is still the simple combination of silver and chloride ions represented by equation (8).

Just as all solutions containing chloride ions will show the property characteristic of that ion,—to form a precipitate with the silver ion,—so the properties characteristic of other ions will be shown by all solutions containing those ions. The copper ion, for example, has a characteristic blue color, and this blue color of the copper ion is shown by all solutions of copper salts, unless the negative ion is also colored. Similarly all permanganates are purple, owing to the color of the permanganate ion (MnO_4^-), all chromates show the yellow of the chromate ion (CrO_4^{--}), etc.

Heat Changes on Mixing Solutions of Ions · Before the formulation of the theory of ionization, chemists were puzzled by the fact that when sodium nitrate solution was added to potassium chloride solution, there was no heat absorbed or given off, although when the solution was evaporated sodium chloride crystallized out. It looked, therefore, as if a chemical reaction had occurred:

$$NaNO_3 + KCl \longrightarrow NaCl + KNO_3 \qquad (9)$$

But chemical reactions commonly involve energy changes, and this one did not. The explanation is that there are no compounds present in a mixture of sodium nitrate and potassium chloride solutions, but only the

ions Na^+, Cl^-, K^+, NO_3^-, not combined with anything; these ions were present originally, and there is no chemical reaction, and consequently no heat change, on mixing. Sodium chloride crystallizes out on evaporation simply because sodium chloride happens to be the least soluble of the four possible ionic crystals which might be formed by pairing the positive and negative ions differently.

Completion of Ionic Reactions · Mention has been made of the fact that many reactions are reversible. If the reverse reaction is to take place, the reaction products must remain at the scene of the reaction; conversely, if the reaction products leave the reaction mixture, the reaction proceeds to completion. If the reaction mixture is a solution of ions, the ions may leave the solution as an insoluble precipitate; hence, the formation of silver chloride, for example, is complete (equation 7). There are other ways in which ions may leave a solution, with consequent completion of the reaction.

Summary of Theory of Ionization · 1. Solutions of electrolytes contain particles called ions. 2. Ions are atoms or radicals that carry electrical charges. 3. The sum of the positive charges equals the sum of the negative charges. 4. In weak electrolytes an equilibrium exists between the nonionized and the slightly ionized parts. Strong electrolytes, although completely ionized, may appear not to be because of strong electrostatic attractions between oppositely charged ions.

Electrochemistry

Electrolysis · We have shown that the mechanism of electrolytic conduction consists in the transport of ions through a solution toward the electrodes of opposite charge. For example, in a moderately concentrated solution of hydrochloric acid in which platinum electrodes are used (Fig. 13-4), the positively charged hydrogen ions move toward the negative electrode (called the *cathode*; the positive ions attracted by it are called *cations*), and the negative chloride ions (*anions*) are attracted to the positive electrode (*anode*). When they

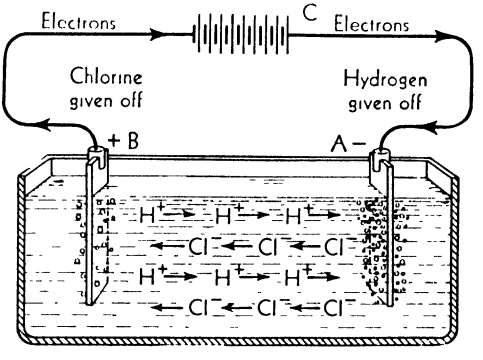


Fig. 13-4. A Diagram Illustrating the Theory of the Electrolysis of a Solution of Hydrogen Chloride

reach the cathode, the hydrogen ions take electrons away from it and become hydrogen atoms, which pair up to escape as gaseous hydrogen:

$$2\,H^+ + 2\,e^- \longrightarrow H_2 \text{ (reduction at the cathode, } A\text{, Fig. 13-4)} \quad (10)$$

Similarly the negative chloride ions give up electrons to the anode, becoming chlorine atoms, which pair up to escape as molecular chlorine gas:

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \text{ (oxidation at the anode, } B\text{, Fig. 13-4)} \quad (11)$$

As shown by the equations, the cathode is the electrode at which reduction occurs; the anode is the electrode at which oxidation occurs, and at which electrons enter the external circuit. The electric circuit is completed by the battery, which acts much as a pump, taking electrons away from the anode and pumping them along through the wire to the cathode. There is no net gain or loss of electrons, but simply a transfer of them from chloride ions through the battery to hydrogen ions. The net result is to carry out the electron-transfer (oxidation-reduction) reaction

$$2\,H^+ + 2\,Cl^- \longrightarrow H_2 + Cl_2 \quad (12)$$

in which the chloride ions give up their electrons to the hydrogen ions.

When a current is passed through melted sodium chloride, similar phenomena occur. The sodium ions are attracted to the cathode, and there take up electrons to become atoms of metallic sodium:

$$Na^+ + e^- \longrightarrow Na \text{ (cathode reaction; reduction)} \quad (13)$$

The chloride ions behave as before, becoming chlorine molecules at the anode:

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \text{ (anode reaction; oxidation)} \quad (11)$$

Since there is no net gain or loss of electrons, the number of electrons taken up by sodium ions is equal to the number given up by chloride ions, and the over-all oxidation-reduction reaction is

$$2\,Na^+ + 2\,Cl^- \longrightarrow 2\,Na + Cl_2 \quad (14)$$

Note that this is the reverse of the reaction which would take place spontaneously if chlorine gas were passed over sodium; it is made to go in this reverse direction by the action of the battery in "pumping" the electrons around the circuit.

A chemical reaction like the one described, resulting from the passage of an electric current through a solution or melt, is called *electrolysis.*

Electrode Reactions · Outside an electrolysis cell the current flows by metallic conduction through the connecting wires; in the solution inside the cell it flows by electrolytic conduction. The change-over from

metallic to electrolytic conduction occurs at the surface of the electrodes and always results in chemical reaction, forming atoms from ions or ions from atoms. The exact nature of the electrode reactions depends upon the nature of the electrolyte and its concentration, the nature of the electrode, the temperature, etc. For example, the electrolysis of a *dilute* solution of hydrochloric acid with platinum electrodes will produce hydrogen gas at the cathode, as does a concentrated solution, but, in place of chlorine, oxygen is produced at the anode, the hydroxyl ions of the water being neutralized rather than the chloride ions:

$$4\ OH^- \longrightarrow 2\ H_2O + O_2 + 4\ e^- \qquad (15)$$

The electrolysis of a sodium chloride *solution* will produce hydrogen and chlorine, the hydrogen ions of the water being discharged rather than the sodium ions. In other cases more than one reaction may go on at an electrode at the same time, so that a mixture of products is obtained.

Applications of Electrolysis · An important electrode reaction is that which results in the formation of metallic atoms at the surface of an electrode. This reaction occurs in electroplating, electrotyping, electrorefining, and electroreduction.

In *electroplating* the objective is to cover the surface of a metallic article with a thin coating of a second metal either as a protection against corrosion or to improve its appearance. A salt of the metal to be deposited is the electrolyte in water solution; and if it gives simple metallic ions, they are deposited on the cathode. The article to be plated is used as the cathode, and the current is passed through the electrolyte until a covering of the desired thickness is produced (Fig. 13-5). Metals high in the electro-chemical series cannot be deposited from an aqueous solution under any ordinary conditions.

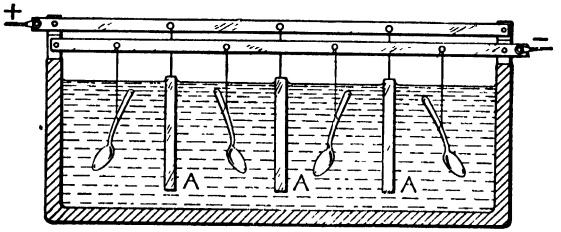


Fig. 13-5. Silver Plating · The article to be plated is made the cathode, plates of silver (*A*) the anode, and a soluble silver salt the electrolyte

The metal may be deposited in the form of a closely adhering layer or a porous powder or a growth of crystals. These variations depend on many factors, including the nature of the metal, the electrolyte used, the temperature, the concentration, the relative surface areas of the electrodes (current density), the voltage, and the rate of deposit. In any given case, conditions must be varied until the desired result is secured.

Oftentimes the presence of foreign materials called *addition agents* has a very desirable effect.

In some cases it is desired to build up a complete object by electrolytic deposit, rather than merely to cover a surface. The most familiar example of this is the process of *electrotyping*, by which the plates from which these pages were printed were made. The page is first set up in type. The face of the type is pressed into wax until a clear impression is obtained. The impressed side of the wax is dusted with fine graphite, polished with a brush, and made the cathode in an electrolytic cell containing a copper salt in solution. The copper is deposited as a thin sheet upon the letters in wax and, when detached, is a perfect copy of the type. Since the underpart of the letters is hollow, the sheet is strengthened by pouring on the undersurface a suitable amount of commercial lead. The sheet so strengthened is then used in printing.

In *electrorefining* an impure metal is purified by causing it to dissolve at the anode, pass through the solution as ions, and deposit as pure metal on the cathode. In the electrorefining of copper a plate of crude copper is made the anode in a solution containing copper sulfate and sulfuric acid, and a thin plate of pure copper is made the cathode. When a current is passed through the solution, copper atoms give up electrons to the anode, and go into solution as copper ions:

$$Cu \longrightarrow Cu^{++} + 2\,e^- \text{ (anode reaction)} \qquad (16)$$

These electrons move through the external circuit to the cathode, and there neutralize copper ions attracted to it:

$$Cu^{++} + 2\,e^- \longrightarrow Cu \text{ (cathode reaction)} \qquad (17)$$

The copper atoms thus formed deposit on the cathode plate as pure copper. The conditions of the electrolysis are adjusted so that the metallic impurities in the crude copper either do not go into the solution, dropping to the bottom of the tank as an "anode sludge," or go into solution but do not deposit on the cathode. In many cases valuable materials can be recovered from the anode sludge.

The purpose of the process of *electroreduction* is to prepare a metal from its compounds. If the metal is not too high in the electrochemical series, an electrolysis of a water solution of a compound may be carried out, as in the case of zinc. Zinc ores are often leached out with sulfuric acid, and the zinc sulfate solution formed is electrolyzed with a pure zinc cathode.

With metals that decompose water readily, a melted electrolyte is used. The electrolysis of fused sodium chloride, discussed on page 216, is used commercially for the preparation of sodium metal.

More rarely some suitable compound of a metal is *dissolved* in one of its fused salts, so that the electrolysis is more like that of an aqueous solution. We shall find this to be the case with aluminum.

The electrolysis of a fused salt presents many practical difficulties. Necessarily the operation is carried on at a moderately high temperature, and the metal liberated is likely to be liquid and very active. It is difficult to protect it from the oxygen and nitrogen of the air. A fused salt is very corrosive and will soon destroy almost any material of which the cell walls are constructed. The oxygen or chlorine evolved at the anode is also very active and must be kept away from the depositing metal. It is because of details such as these that the electrometallurgy of each metal requires its own form of apparatus. The actual liberation of the metal usually presents no great difficulty. There is therefore room for great inventive skill in the design of apparatus to fit each particular case.

Faraday's Laws · The laws governing the amount of material undergoing reaction in an electrolysis were discovered by Faraday in his early researches on electrolytic conduction. Faraday observed that the weight of hydrogen or oxygen or silver or other element liberated at an electrode depends *solely* on the *quantity of electricity* that flows through the solution undergoing electrolysis. It does not depend at all on the temperature or the concentration of the solution, or the rate at which the charge flows, but only on the *quantity of electricity*. This fact constitutes Faraday's first law: *The amount of electrochemical change is directly proportional to the quantity of electricity that flows* (Fig. 13-6).

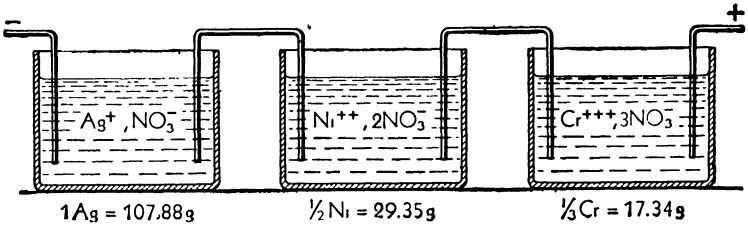


Fig. 13-6. Illustration of Faraday's Laws · To deposit the metallic *atoms* Ag, Ni, Cr from the solutions of the salts in which they occur as the *ions* Ag^+, Ni^{++}, Cr^{+++}, each Ag^+ ion must recover 1 electron, each Ni^{++} ion 2 electrons, and each Cr^{+++} ion 3 electrons. One *faraday* of electricity furnishes enough electrons to silver ions to deposit 1 g-at. wt (1 g-equiv wt) of silver, but it can provide electrons for only ½ g-at. wt of nickel (1 g-equiv wt) and only ⅓ g-at. wt of chromium (1 g-equiv wt). A given current will deposit these three metals from solution in the *ratio* of their gram-equivalent weights (107.88 g Ag; 29.35 g Ni; 17.34 g Cr), whether the quantity of current passing consists of 100 electrons or of 100 billion

Faraday's second law has to do with the relation between the relative weights of the *different elements* liberated at the electrodes by the *same* quantity of electricity, and the gram-equivalent weights of those elements.

The *gram-equivalent weight* of an element is its gram-atomic weight divided by its valence. Faraday's experiments proved that *if a given quantity of electricity is allowed to flow successively through a number of different solutions in series, the weights of the various elements liberated at the electrodes are in the ratio of their gram-equivalent weights* (Fig. 13-6).

The Avogadro Number · The explanation of Faraday's laws in the light of our present knowledge is obvious. Since the electrode reactions involve gain or loss of electrons, it is evident that the amount of material deposited depends only upon the number of electrons which pass around the circuit, that is, upon the quantity of electricity which passes around the circuit, and not upon the temperature or other conditions of the electrolysis. Further, since the charge on an ion determines the number of electrons that need to be gained or lost to neutralize it, the number of ions of different elements, such as Ag^+, Ni^{++}, and Cr^{+++}, which can be neutralized by a given number of electrons will vary inversely as the charges. The weights of the elements deposited (Fig. 13-6) at the electrode will equal the number of atoms times the weight of the atom; since the number of atoms deposited is inversely proportional to the charge on their ions, the weights of the elements deposited must be in the ratio of their equivalent weights (atomic weights divided by valence).

An electrolysis, in other words, essentially counts the number of electrons which pass through the circuit. This fact makes it possible to calculate the Avogadro number from electrolysis experiments. It is found experimentally that a quantity of electricity amounting to 96,488 coulombs is required to liberate 1 g-equiv wt of an element. This quantity (called a faraday) is the same for any element, by Faraday's second law. For a univalent element such as silver, the gram-equivalent weight is equal to the gram-atomic weight, and it follows that the passage of 96,488 coulombs will produce 1 g-at. wt of silver. The charge on an electron is 1.6020×10^{-19} coulomb; hence the passage of 96,488 coulombs represents the passage of $\frac{96{,}488}{1.6020 \times 10^{-19}} = 6.023 \times 10^{23}$ electrons around the circuit. Each electron neutralizes one silver ion:

$$Ag^+ + e^- \longrightarrow Ag \qquad (18)$$

so that the number of silver atoms in a gram-atomic weight is 6.02×10^{23}. This is the calculation of the Avogadro number, promised on page 138.

Electrical Units · The unit of resistance, the *ohm*, was formerly defined as the resistance at 0° of a column of mercury 106.300 cm in length, and of such cross section (about 1 mm^2) that it weighs 14.4521 g. The unit of quantity is the *coulomb*; and it was the quantity of electricity required to liberate exactly 0.001118 g

of silver. The *ampere* (amp) is the unit of current and is defined as the flow of current equal to 1 coulomb/sec. When the electromotive force (potential) is of such a value that it can drive a current of 1 amp through a resistance of 1 ohm, it is said to have the unit value of 1 *volt* (v). As of January 1, 1948, a modified method of defining these units was adopted, and the size of the units changed slightly. As compared with the old units, given above, the new ampere is 1.00017 times larger, the new volt 0.99967 as large, and the new ohm 0.99951 as large. The differences become significant only in measurements of high precision.

Batteries · Since an electric current, in passing through a solution, causes an electron-transfer reaction to take place, it is only natural to wonder whether the electrochemical effect can be reversed. Can we set up an apparatus so that the electrons transferred in a reaction can be made to flow through a wire in an external circuit and thus produce an electric current? The answer is Yes. Such an arrangement, in which a chemical reaction produces electrical energy, is called a *galvanic cell* or *battery*.

Properly speaking, a cell consists of an electrolyte and a single pair of electrodes, while a battery is usually a group of such cells.

Acid Cell · If zinc is added to sulfuric acid, zinc sulfate and hydrogen are formed.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \tag{19}$$

$$Zn + 2\,H^+ + SO_4^{--} \longrightarrow Zn^{++} + SO_4^{--} + H_2 \tag{20}$$

Since sulfuric acid and zinc sulfate are electrolytes, the reaction is actually that between zinc and the hydrogen ion to form the zinc ion and hydrogen:

$$Zn + 2\,H^+ \longrightarrow Zn^{++} + H_2 \tag{21}$$

the sulfate ion playing no part in the reaction. This is an electron-transfer reaction; the zinc atoms lose electrons, becoming zinc ions:

$$Zn \longrightarrow Zn^{++} + 2\,e^- \tag{22}$$

and the hydrogen ions gain electrons, becoming hydrogen atoms, which pair up to form diatomic molecules:

$$2\,H^+ + 2\,e^- \longrightarrow 2\,H \longrightarrow H_2 \tag{23}$$

If this reaction is carried out by dipping a zinc rod into sulfuric acid, hydrogen bubbles form on the surface of the zinc, and a noticeable amount of heat is produced by the reaction (Fig. 13-7, *A*). Now let us introduce a graphite rod into the solution, along with the zinc (Fig. 13-7, *B*), not allowing the two rods to touch. The graphite rod has no effect, hydrogen continues to escape from the zinc, and heat is still generated. But if we now join the zinc rod to the graphite rod with a metallic conductor (say, a copper wire) in an external circuit containing a resistance (Fig. 13-7, *C*), two profound changes in the whole process take place: (1) While the zinc

continues to dissolve, *the hydrogen now bubbles off from the graphite rod.* (2) *The heat generated is much less than before;* and with the use of a suitable electric measuring instrument, we find that *an electric current is flowing* through the wire from one rod to the other.

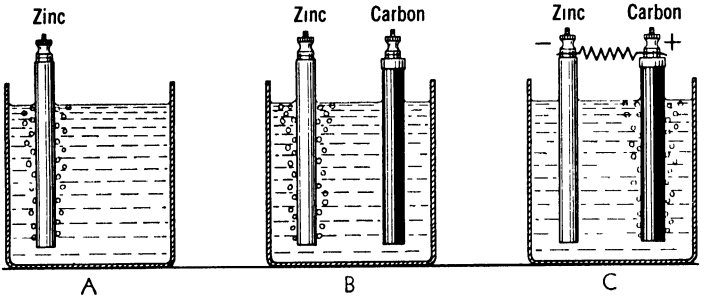


Fig. 13-7. Diagrams of Details of an Acid Cell

Interpretation of the Changes Taking Place in an Acid Cell · Our interpretation of these changes is as follows: The zinc atoms continue to dissolve as zinc ions; but their electrons, instead of being handed over directly to the hydrogen ions, push their way from the negatively charged zinc rod by way of the external circuit and onto the surface of the graphite rod, where the hydrogen ions in the solution find it easier to pick off the electrons (and become hydrogen atoms) than at the zinc surface. Exactly the same chemical reaction occurs as before. However, the energy liberated in the chemical reaction, which previously appeared entirely as heat, is now transformed in part into the electrical energy of the moving electrons, and the decrease in the amount of heat energy is exactly equivalent to the electrical energy generated.

The zinc rod, where oxidation occurs, is the anode and is the negative pole of the cell; the graphite rod, where reduction occurs, is the cathode and is the positive pole. The electric current (the stream of electrons) flows from the negative pole through the wire to the positive pole. However, it is still common practice to speak of the current as flowing from the positive pole to the negative, because of the survival of an old convention, adopted long before much was known about the nature of electricity.

Polarization · The acid cell just described is not very efficient. It will function well for a brief time, but soon the hydrogen gas liberated at the graphite electrode forms a film on it that effectively insulates the graphite from the solution and builds up such a high resistance that the current virtually ceases to flow. An electrode in this condition is said to be *polarized.* It is evident that an effective cell must be provided with some way for preventing the formation of a film of hydrogen at the electrode.

Dry Cell · The widely used *dry cell* acts in essentially the same manner as the acid cell. A zinc vessel, *A* (Fig. 13-8), containing a mixture of 90% manganese dioxide and 10% carbon black moistened with a solution of ammonium chloride, *B*, *B*, acts as the negative pole. The positive pole is a graphite rod, *C*, surrounded by manganese dioxide, *E*. When the negative and positive poles are connected with a wire, an electron-transfer reaction takes place. The zinc (anode) is oxidized and dissolves as Zn^{++} ions; the electrons set free flow through the wire to the graphite (cathode), where the manganese dioxide is reduced in the presence of the NH_4^+ ions.

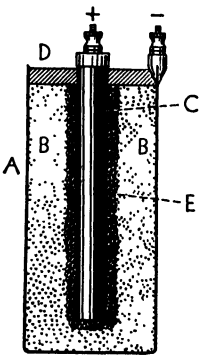


Fig. 13-8. Vertical Section of a Dry Cell

$$(-)\ \text{pole:}\ Zn \longrightarrow Zn^{++} + 2\,e^- \qquad (22)$$

$$(+)\ \text{pole:}\ 2\,NH_4^+ + 2\,MnO_2 + 2\,e^- \longrightarrow 2\,NH_3 + H_2O + Mn_2O_3 \qquad (24)$$

With small currents, for but brief time intervals, little polarization occurs, but large currents and continuous use result in polarization. Millions of these cells are used annually for operating such devices as doorbells, flash lights, telephones, and portable radio sets. Were it not for the manganese dioxide, hydrogen would be evolved, as in the acid cell.

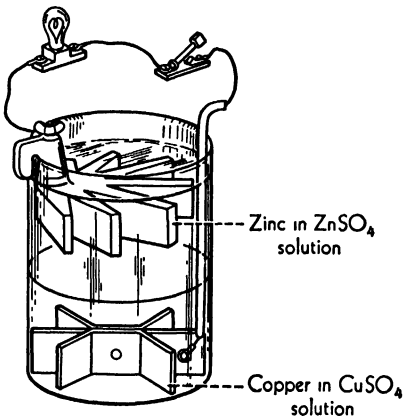


Fig. 13-9. The Daniell Cell

Daniell Cell · In the days before the electric dynamo had come into wide use, the Daniell cell (or crowfoot cell, as it was called) was one of the chief sources of electric current, and many thousands of miles of telegraph lines were operated by these cells. It consists of a jar with an electrode of thin sheet copper at the bottom, covered with a saturated solution of copper sulfate (Fig. 13-9). A solution of zinc sulfate floats on the denser copper sulfate solution, and in this is immersed a zinc electrode. When the external circuit is completed, electrons flow from the zinc through the wire to the copper.

At the negative (zinc) electrode the reaction is

$$Zn \longrightarrow Zn^{++} + 2\,e^- \qquad (22)$$

At the positive electrode the reaction is

$$Cu^{++} + 2\,e^- \longrightarrow Cu \qquad (17)$$

so that the over-all reaction is

$$Zn + Cu^{++} \longrightarrow Zn^{++} + Cu \qquad (25)$$

This, of course, is the reaction which would be predicted, since zinc is above copper in the electrochemical series and consequently displaces copper from copper compounds. As a result of this reaction, the zinc electrode gradually dissolves in use, and the copper electrode increases in weight, owing to the copper deposited on it. The electrons given up by the zinc atoms flow through the external circuit to the copper electrode and there neutralize copper ions. The electric circuit is completed within the cell by the movement from the copper sulfate solution of sulfate ions, which, deserted by the copper ions, move across the boundary between the solutions and pair off with the newly formed zinc ions.

Reactivity · Cells such as those described above can in theory be constructed for any chemical reaction which involves an electron transfer. The voltage of such cells depends not at all on the size or shape of the electrodes, or on the distance separating them, but only on the nature of the electrodes, the composition of the solutions, and the temperature. The cells constructed may be of little practical importance. From the theoretical standpoint, however, they are of great importance, since the voltage of such a cell is a quantitative measure of the reactivity of the reacting substances, a measure of the driving force of the chemical reaction.

Standard Electrode Potentials · The electrochemical series of the metals gives us a qualitative measure of the reactivities of the metals relative to one another. It is now seen from the examples given (zinc plus sulfuric acid, zinc plus copper sulfate) that the displacement of one metal by another, discussed on page 87, is in every case an electron-transfer reaction. Therefore a quantitative measure of the reactivities of the metals can be made by setting up cells similar to the Daniell cell for each metal pair, with each metal immersed in a solution of its own ions.

Just as the *reaction* taking place in such a cell may be separated into two electrode reactions, at the cathode and anode, so the *voltage* of the cell is by convention considered to be the sum of a voltage associated with the cathode reaction and a voltage associated with the anode reaction. It is not possible to measure these voltages separately, since every cell must obviously contain both a cathode and an anode; however, numerical values can be assigned to the individual electrode reactions by

assigning an arbitrary value to some electrode reaction chosen as a standard. The convention adopted is that the voltage, or potential, corresponding to the reaction

$$H_2 \rightleftarrows 2\,H^+ + 2\,e^-$$

is zero for the reaction proceeding in either direction, when the hydrogen-ion concentration is 1 molal.

Potentials of other electrode reactions are measured against this standard by pairing the other electrodes in cells with a hydrogen electrode. Since hydrogen, being gaseous, cannot of itself serve as a conducting electrode, a chemically inert electrode, such as platinum, which absorbs hydrogen readily, is used, and while in use is kept bathed in an atmosphere of hydrogen.

The electron-transfer reaction between zinc metal and hydrogen ions can be used under the above convention to measure the potential for the oxidation of zinc to zinc ions. A cell is constructed in which a zinc rod is immersed in a solution of zinc ions at 1 molal concentration, and paired with a standard hydrogen electrode. The direction of flow of current is determined electrically, and it is found that electrons are flowing from the zinc rod through the wire to the platinum of the hydrogen electrode. Hence the zinc is being oxidized and the hydrogen reduced, and the two electrode reactions are

$$Zn \longrightarrow Zn^{++} + 2\,e^- \qquad 2\,e^- + 2\,H^+ \longrightarrow H_2$$

The voltage of the cell is considered to be the sum of the voltages corresponding to the two electrode reactions, or

$$E_{cell} = E_{Zn \rightarrow Zn^{++}} + E_{2\,H^+ \rightarrow H_2}$$

By the convention that the hydrogen voltage, $E_{2H^+ \rightarrow H_2}$, is zero, the measured voltage of the cell, 0.762 v, is assigned to the oxidation reaction of zinc, and is called the standard oxidation electrode potential of zinc.

By a series of measurements of this sort a table (p. 227) of standard oxidation electrode potentials can be obtained, not only for the formation of ions from metals but for other electrode reactions as well. All the values in the table are obtained with 1 molal concentrations of all the reacting ions in water solution, and with hydrogen and other gases at atmospheric pressures.

The electrode reactions are all written as oxidation reactions. By convention we use the positive sign to indicate that the element is oxidized more readily than hydrogen; the negative sign to indicate that the

element is oxidized less readily than hydrogen. Thus in the cell above, containing zinc and hydrogen, the oxidation potential of the zinc is given a plus value in the table (p. 227).

If a cell using copper instead of zinc

Copper	Hydrogen
electrode in copper ions	electrode in hydrogen ions

is constructed for measuring the standard electrode potential of copper, the direction of flow of current shows that electrons are flowing toward the copper from the hydrogen electrode. This means that the copper is oxidized less readily than hydrogen. The electrode reactions are

$$H_2 \longrightarrow 2\,H^+ + 2\,e^- \qquad 2\,e^- + Cu^{++} \longrightarrow Cu$$

and the voltage is

$$E_{cell} = E_{H_2 \rightarrow 2\,H^+} + E_{Cu^{++} \rightarrow Cu}$$

Again the hydrogen voltage is called zero; the total voltage of the cell, 0.340 v, is assigned to the copper electrode; and the oxidation potential in the table (p. 227) is -0.340 v.

From the values in the tables we can calculate the voltage of any cell in which the recorded electrode reactions take place. For the Daniell cell, for example, we want the values for the reactions

$$Zn \longrightarrow Zn^{++} + 2\,e^- \quad \text{and} \quad 2\,e^- + Cu^{++} \longrightarrow Cu$$

The value for the oxidation reaction of zinc is given in the table, but the table also gives the *oxidation* reaction for copper. To get the value for *reduction* of copper ion we must change the sign of the value given in the table, and

$$E_{\text{Daniell cell}} = E_{Zn \rightarrow Zn^{++}} + E_{Cu^{++} \rightarrow Cu} = E_{Zn \rightarrow Zn^{++}} - E_{Cu \rightarrow Cu^{++}}$$
$$= 0.762 - (-0.340) = 1.107 \text{ v.}$$

This value corresponds to 1-molal ion concentrations; in actual use the concentrations are different from this, and the voltage is about 1 volt.

The sign of the oxidation potential does not show whether the electrode is the positive or negative pole of a battery; this depends upon what the other electrode is. Thus if a zinc electrode is placed in a cell with the hydrogen electrode, electrons flow from the zinc to the hydrogen electrode, and the zinc rod must be connected as the negative pole. However, in a cell containing a zinc and a magnesium electrode, electrons flow toward the zinc from the magnesium, and the zinc rod must be connected as the positive pole. The electrode reactions in the zinc-magnesium cell are as follows:

$$2\,e^- + Zn^{++} \longrightarrow Zn \qquad Mg \longrightarrow Mg^{++} + 2\,e^-$$

and the voltage, for 1-molal concentrations, is

$$E_{cell} = E_{Zn^{++} \rightarrow Zn} + E_{Mg \rightarrow Mg^{++}} = - E_{Zn \rightarrow Zn^{++}} + E_{Mg \rightarrow Mg^{++}} =$$
$$. \; - 0.762 + 2.34 = 1.578 \text{ v.}$$

STANDARD OXIDATION ELECTRODE POTENTIALS

ELECTRODE REACTION	POTENTIAL (VOLTS)
1. $Na \longrightarrow Na^+ + e^-$	2.712
2. $Mg \longrightarrow Mg^{++} + 2\,e^-$	2.34
3. $Al \longrightarrow Al^{+++} + 3\,e^-$	1.67
4. $Zn \longrightarrow Zn^{++} + 2\,e^-$	0.762
5. $Fe \longrightarrow Fe^{++} + 2\,e^-$	0.440
6. $Pb + SO_4^{--} \longrightarrow PbSO_4 + 2\,e^-$	0.355
7. $Ni \longrightarrow Ni^{++} + 2\,e^-$	0.250
8. $Pb \longrightarrow Pb^{++} + 2\,e^-$	0.126
9. $H_2 \longrightarrow 2\,H^+ + 2\,e^-$	0.000
10. $Sn^{++} \longrightarrow Sn^{++++} + 2\,e^-$	− 0.15
11. $Bi \longrightarrow Bi^{+++} + 3\,e^-$	− 0.20
12. $Cu \longrightarrow Cu^{++} + 2\,e^-$	− 0.345
13. $2\,I^- \longrightarrow I_2 + 2\,e^-$	− 0.535
14. $Fe^{++} \longrightarrow Fe^{+++} + e^-$	− 0.771
15. $Ag \longrightarrow Ag^+ + e^-$	− 0.800
16. $2\,Br^- \longrightarrow Br_2 + 2\,e^-$	− 1.087
17. $Mn^{++} + 2\,H_2O \longrightarrow MnO_2 + 4\,H^+ + 2\,e^-$	− 1.28
18. $2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$	− 1.358
19. $Mn^{++} + 4\,H_2O \longrightarrow MnO_4^- + 8\,H^+ + 5\,e^-$	− 1.52
20. $PbSO_4 + 2\,H_2O \longrightarrow PbO_2 + 4\,H^+ + SO_4^{--} + 2\,e^-$	− 1.685
21. $2\,F^- \longrightarrow F_2 + 2\,e^-$	− 2.85

Storage Batteries · In dry cells and the Daniell cell the zinc electrodes waste away, and the electrolyte is soon exhausted. In a storage battery, on the other hand, we can reverse the chemical reaction which takes place by subjecting the contents of the cell to an electrolysis, using a current from an outside source. This electrolysis restores the cell to its original condition, so that it can again serve as a source of current.

Lead Storage Battery · The storage battery used in automobiles is represented in Fig. 13-10. A number of lead plates covered with a deposit of lead in spongy condition are joined by a crossbar, as shown at *A*. An equal number of lead plates covered with lead dioxide (PbO_2) are similarly joined by a bar, at *B*. These two sets of plates are arranged in the electrolyte of sulfuric acid in such a way that the plates alternate with each other but do not touch.

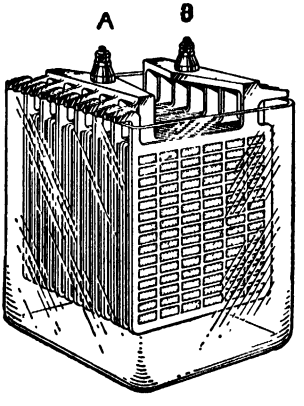


Fig. 13-10. A Seven-Plate Storage Battery

The reaction at the plate covered with spongy lead, when the cell is being discharged, is as follows:

$$Pb + SO_4^{--} \longrightarrow PbSO_4 + 2\,e^- \qquad (26)$$

The insoluble lead sulfate deposits in the spongy lead, and the two electrons are given up to the plate, which is thus the negative electrode. These electrons flow through the electric circuit to the lead dioxide plate, where the reaction is

$$PbO_2 + SO_4^{--} + 4\,H^+ + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O \qquad (27)$$

Lead sulfate deposits on the plate, and two electrons are taken from the plate. From the table on page 227 it is seen that the voltage, for normal concentration of the hydrogen ion, would be $0.355 - (-1.685) = 2.040$ v. In practice the sulfuric acid is more concentrated than this, and the voltage is somewhat greater than 2 v. Three or six such cells are used in series to give the 6 v or 12 v required for automobiles and trucks. The complete chemical reaction is

$$Pb + PbO_2 + 2\,H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2\,PbSO_4 + 2\,H_2O \qquad (28)$$



Fig. 13-11. A Type of Hydrometer Used for Measuring the Density of the Acid Solution in the Lead Storage Battery

As the cell delivers current, the two electrodes approach an identical condition by the deposit of lead sulfate on both. At the same time sulfuric acid is withdrawn from the electrolyte, which in consequence diminishes in density. The latter fact permits the condition of the cell to be judged by measuring the density of the sulfuric acid with a simple hydrometer (Fig. 13-11).

As indicated in equation (28), the cell reaction is reversible. When a current from a dynamo is passed through the cell in the opposite direction, the electrolysis causes the lead sulfate to be changed to lead, lead dioxide, and sulfuric acid, storing up the electrical energy in these chemical substances for use again in producing current by their spontaneous reaction.

Other Batteries · There are several different kinds of storage batteries now in use. Among these the Edison storage battery is better suited for many purposes than the lead storage battery, chiefly because it is more rugged and will stand more abuse than the lead cell. It consists of a nickel electrode covered with nickelic oxide as the positive electrode, and an iron electrode as the negative electrode, immersed in sodium hydroxide solution. When the cell is producing current, the reaction is

$$NiO_2 \cdot 2\,H_2O + Fe \longrightarrow Fe(OH)_2 + Ni(OH)_2 \qquad (29)$$

The voltage of the Edison cell is about 1.3 v.

The recently-developed nickel-cadmium cell, which also has a voltage of about 1.3, has an exceptionally long life and can be used at low temperatures.

QUESTIONS

1. What is meant by the following terms; (*a*) *ion;* (*b*) *electrolytic conduction;* (*c*) *metallic conduction;* (*d*) *interionic attraction;* (*e*) *electrolysis;* (*f*) *cathode;* (*g*) *anode;* (*h*) *oxidation;* (*i*) *reduction;* (*j*) *strong* and *weak electrolytes?*

2. How can the following facts be accounted for?

a. A molal solution of sodium chloride has a lower freezing point than a molal solution of sugar.

b. A molal solution of sugar has the same freezing point as a molal solution of alcohol.

c. The freezing-point lowering due to the addition of a gram-formula weight of sodium chloride to 1000 g of water is not twice as much as that produced by the addition of a gram-molecular weight of alcohol.

d. Ammonia, a *covalent* compound, dissolves in water to form a solution which is an excellent conductor of the electric current.

e. Sodium atoms react with water, but sodium ions do not.

f. Hydrochloric acid will dissolve zinc but not copper.

g. The reaction of oxygen with copper to form copper oxide, and with chlorine to form copper chloride, are both processes in which oxidation occurs.

h. When oxidation occurs, there is an equivalent amount of reduction.

i. A battery may be considered an electron pump.

3. Write the equations for the reactions that occur at each electrode of (*a*) a dry cell; (*b*) a lead storage battery which is being charged; (*c*) a lead storage battery which is furnishing current.

4. Give a brief sketch of the life of (*a*) Faraday; (*b*) Volta; (*c*) Ampère. (Consult an encyclopedia.)

5. Draw a diagram of the complete circuit used for the electrolysis of a solution of sodium chloride; indicate all reactions that occur and the type of conduction in the various parts of the circuit.

6. How does the theory of ionization explain

a. The conductivity of a solution of sodium chloride?

b. The precipitation of the same substance when silver nitrate solution is added to a sodium chloride, a potassium chloride, or an ammonium chloride solution?

c. The similarity of color of dilute solutions of copper sulfate, copper nitrate, and copper chloride?

d. The green color of copper chromate solutions?

e. The difference between the conduction of an electric current by potassium chloride and acetic acid solutions of the same concentration?

f. The increase in the ratio of the freezing-point lowering for potassium chloride to the freezing-point lowering for sugar, with increasing dilution?

g. The increase in the ratio of the freezing-point lowering for acetic acid to the freezing-point lowering for sugar, with increasing dilution?

PROBLEMS

1. Complete the ionic equations for the following reactions: (*a*) $Zn + Cu^{++} \longrightarrow$; (*b*) $Zn + Ag^{+} \longrightarrow$; (*c*) $Mg + H^{+} \longrightarrow$; (*d*) $Mg + Ag^{+} \longrightarrow$; (*e*) $Fe + Ni^{++} \longrightarrow$; (*f*) $Cu + Ag^{+} \longrightarrow$. From the data in the table on page 227 calculate the voltages of the cells in which these reactions take place.

2. A current of electricity was passed through a solution of a salt of each of the following metals: (*a*) silver; (*b*) nickel (bivalent); (*c*) chromium (trivalent). The weight of silver deposited was 84.6 g. Calculate the weight of each of the other metals deposited.

3. (*a*) If 1 coulomb of electricity will deposit 0.001118 g of silver, calculate the number of coulombs required to deposit 1 g-equiv wt of silver. (*b*) How many coulombs are there in a faraday?

4. Calculate the weights in grams of the following ions which would be deposited from their solutions by 0.05 faraday: (*a*) Ag^{+}; (*b*) Cu^{+}; (*c*) Cu^{++}; (*d*) Al^{+++}; (*e*) Au^{+}; (*f*) Au^{+++}.

5. If a current of 0.1 amp passes through an aqueous sodium chloride solution for 10 minutes, what *weight* of chlorine gas will be liberated at the anode?

6. How long must a current of 1 amp be passed through acidulated water in order to produce 1 liter of *dry* hydrogen gas measured at 27° and 745 mm?

7. When a current of 1 amp is flowing through a wire, how many electrons pass a given point on the wire per second?

8. If a Daniell cell operates just long enough to allow 1 g-at. wt of zinc to dissolve at the negative electrode and 1 g-at. wt of copper to deposit at the positive electrode, how much electrical energy is furnished by the cell if the voltage is 1.10 v?

CHAPTER 14

ACIDS, BASES, AND SALTS

Introduction · In Chapter 5 we observed that some oxides dissolve in water to form *acids*, while others dissolve to form *bases*; for example,

$$CO_2 + H_2O \longrightarrow H_2CO_3 \text{ (carbonic acid)}$$
$$Na_2O + H_2O \longrightarrow 2\,NaOH \text{ (sodium hydroxide, a base)}$$

Acids and bases react to form *salts*, and these three important classes of compounds are electrolytes. Common table salt (NaCl) is the product of such a reaction between hydrochloric acid (HCl) and the base sodium hydroxide (NaOH). On the other hand, common salt can be used to prepare both sodium hydroxide and hydrochloric acid. We will use common salt to show the relationship between salts, acids, and bases; at the same time we will discuss several important properties of these classes of compounds.

The Chemistry of Common Salt · Common salt (sodium chloride, NaCl) is very widely distributed in nature. Thick strata, evidently formed by the evaporation of salt water, are found in many places. In the United States the most important localities are Michigan, New York, and Ohio. Sometimes the salt is mined as *rock salt*; very often, however, a strong brine is pumped from deep wells driven into the salt deposit, and the brine is then evaporated in large pans until the salt crystallizes. In other places salt is recovered by the evaporation of sea water.

Salt crystals form small cubes, are anhydrous, and melt at 804°. Pure salt does not absorb moisture from the air unless the humidity of the air is at least 75 per cent; but table salt becomes moist in much drier air because of impurities. Salt is essential for animal life, and it is said that the average person consumes about 30 lb annually. It is the source of the hydrochloric acid that constitutes from 0.4 to 0.5 per cent of the human gastric juice.

Industrially salt is used not only as the source of both sodium and chlorine themselves, but also in the preparation of nearly all substances that contain either of these elements. These include many products of the highest importance to civilization, such as soap, glass, hydrochloric acid, sodium carbonate, and bleaching powder. In 1954 over 17,000,000 tons of salt was produced in the United States.

Electrolysis of Sodium Chloride · Sodium chloride is an electrovalent compound (Na^+, Cl^-); and when its crystals are melted or dissolved in water, it is an electrolyte. Under either of these conditions the ions of salt are free to move about, and in an electric field the Na^+ ions move toward the cathode and the Cl^- ions toward the anode. In the melted salt both the sodium ions and the chloride ions are discharged at the electrodes, and metallic sodium and chlorine gas are formed (p. 216). If, however, the electrolysis is carried out in water solution, hydrogen and chlorine are formed at the electrodes. Chlorine is formed at the anode as before, the anion giving up its electron to the electrode:

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \text{ (anode reaction)}$$

At the cathode it is the hydrogen ions, always present in small amount in water solutions as a result of the slight ionization of water,

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

that are discharged, rather than the sodium ions. The reason for this is that, as shown by its position in the electrochemical series, the hydrogen ion has a greater affinity for electrons than the sodium ion, so that in the competition between the two kinds of ions for the electrons furnished by the cathode, the hydrogen ion always wins:

$$2\,H^+ + 2\,e^- \longrightarrow H_2 \text{ (cathode reaction)}$$

The removal of the hydrogen ions leaves the hydroxyl ions (OH^-), so that the ions of sodium hydroxide (NaOH) collect in the solution, and sodium hydroxide may be obtained from it by evaporating off the water. Much of the sodium hydroxide used commercially is prepared in this way.

If the hydrogen formed at the cathode is collected and burned in the chlorine formed at the anode, hydrogen chloride (HCl) is formed. The solution of this substance in water is known as hydrochloric acid. Limited quantities of the hydrochloric acid used commercially are prepared from the gaseous products of the electrolysis in this manner.

Neutralization Reaction · When hydrochloric acid and sodium hydroxide are mixed, sodium chloride is formed:

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

This is a specific example of a general reaction between an *acid* and a *base* to form a *salt* and *water*:

$$\text{Acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

Such a reaction is called a *neutralization reaction*.

Hydrogen Ion and Hydroxyl Ion · The equation for the neutralization reaction between hydrochloric acid and sodium hydroxide, written above, may now be considered in further detail. All the substances, other than water, are strong electrolytes and are present in the solution as ions:

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

When the equation is written in this fashion, it is evident that the sodium ions and the chloride ions have played no part in the reaction, since they were present in the solution both at the beginning and at the end of the reaction. The essential reaction has been

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

From these two ionic equations we can also see that the properties which we associate with acids are due to the presence in acid solutions of an appreciable quantity of hydrogen ions, and the properties which we associate with bases are due to the presence in basic solutions of appreciable quantities of hydroxyl ions. Further, neutralization may be defined as the union (in equivalent quantities) of the hydrogen ions of an acid with the hydroxyl ions of a base to form water molecules.

Acid Properties · What are the properties associated with acids, that is, with hydrogen ions? They may be summarized as follows:

1. **Taste.** Dilute acids have a sour taste, like that of vinegar or lemons or many unripe fruits.

2. **Action on indicators.** Acids cause changes in the color of certain compounds. Thus, they change the color of blue litmus to red and the orange color of methyl orange to red. Compounds like litmus and methyl-orange are called indicators, since they indicate by their colors the presence or absence of acids.

3. **Action on metals.** Metals above hydrogen in the electrochemical series react with acids to form hydrogen and a salt. (Other reactions may occur with a few acids; see Chapter 23.) Thus, hydrochloric acid reacts with zinc:

$$\underset{\text{metal}}{Zn} + 2\,\underset{\text{acid}}{HCl} \longrightarrow \underset{\text{salt}}{ZnCl_2} + \underset{\text{hydrogen}}{H_2}$$

One definition of a salt stems from this reaction—namely, that a salt is a compound in which the hydrogen of an acid has been replaced by a metal. The hydrochloric acid and zinc chloride are electrolytes, and the reaction is that of electron transfer between zinc atoms and hydrogen ions (p. 221):

$$Zn + 2\,H^+ \longrightarrow Zn^{++} + H_2$$

This reaction is similar for all acids, in that all acid solutions contain hydrogen ions.

4. **Action on oxides and hydroxides of metals.** Acids react with oxides and hydroxides of metals to form salts and water. Thus, hydrochloric acid reacts with calcium oxide or calcium hydroxide:

$$2\ HCl + CaO \longrightarrow CaCl_2 + H_2O$$
$$2\ HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\ H_2O$$

Here, again, the actual reagent in the acid solution is the hydrogen ion.

We associate the acid properties above with the hydrogen ion, and we define an acid as *any compound that gives hydrogen ions in solution.*

Replaceable Hydrogen in an Acid · The molecules of various acids are capable of giving different numbers of free hydrogen ions in solution. The number given by a molecule of a specified acid is called the *basicity* of the acid. For example, HCl is a monohydrogen (monobasic) acid; H_2SO_4 is a dihydrogen (dibasic) acid; H_3PO_4 is a trihydrogen (tribasic) acid.

The formulas of some acids, such as acetic acid ($C_2H_4O_2$) and tartaric acid ($C_4H_6O_6$), would apparently indicate a still higher basicity; but experiment shows that in the acetic acid only one hydrogen atom may be replaced by metals, and in tartaric only two. On this account the formulas are often written $HC_2H_3O_2$ and $H_2C_4H_4O_6$.

Specific Properties of Individual Acids · In addition to the properties common to all acids, due to the presence of hydrogen ions, acids have other properties, which may vary widely in individual cases. These properties, specific for each acid, are due to the anion present. Thus, hydrochloric acid will show the properties of the chloride ion (Cl^-), sulfuric acid those of the sulfate ion (SO_4^{--}), phosphoric acid those of the phosphate ion (PO_4^{---}), acetic acid those of the acetate ion ($C_2H_3O_2^-$), etc. Sometimes properties characteristic of undissociated molecules are also observed.

Basic Properties · The hydroxides of the various metals, including sodium hydroxide (NaOH), have many properties in common and as a group are called *bases*. Many hydroxides are insoluble in water; all the soluble ones are white solids. The very soluble bases sodium hydroxide (NaOH) and potassium hydroxide (KOH) are often called *alkalies*.

There are a great many bases, and it is of importance to learn their characteristics as a class of compounds. In general, their solutions (1) taste bitter rather than sour; (2) feel soapy; and (3) reverse the color changes produced in indicators by acids—for example, they turn red litmus blue.

The most distinctive property of bases as a class of compounds is that in water solution all give *hydroxyl ions* (OH^-). Because of this property

we can frame the definition *A base is any compound that gives hydroxyl ions in water solution.* In addition to the properties of the hydroxyl ions, each base has individual properties, owing to the cation present and to any non-ionized molecules of the base.

The Available Hydroxyl Ions of a Base · The formula of the hydroxide of a univalent metal contains only one hydroxyl (OH^-) group; that of a divalent metal, two hydroxyl groups; that of a trivalent metal, three. These facts are sometimes indicated by the phrase *acidity of a base,* meaning the number of hydroxyl groups in the formula and present as free ions in solution, thus:

Monohydroxyl (monoacid) base: $Na^+, OH^- \rightleftarrows Na^+ + OH^-$
Dihydroxyl (diacid) base: $Ca^{++}, 2\,OH^- \rightleftarrows Ca^{++} + 2\,OH^-$
Trihydroxyl (triacid) base: $Al^{+++}, 3\,OH^- \rightleftarrows Al^{+++} + 3\,OH^-$

There are a few tetracid bases, such as stannic hydroxide ($Sn(OH)_4$); but for the most part these lose a molecule of water and act as dihydroxyl bases:

$$Sn(OH)_4 \longrightarrow SnO(OH)_2 + H_2O$$

Heat of Neutralization · We have seen that the essential part of a neutralization reaction is a combination of hydrogen and hydroxyl ions to form water. If this is correct and if the formation of water from its two ions is the only reaction taking place in neutralization of strong acids by strong bases in moderately dilute solution, then the heat of all such reactions should be the same. That this is so is indicated from the equations

$$H^+, Cl^- + Na^+, OH^- \longrightarrow Na^+, Cl^- + H_2O + 13{,}680 \text{ cal}$$
$$H^+, NO_3^- + Na^+, OH^- \longrightarrow Na^+, NO_3^- + H_2O + 13{,}690 \text{ cal}$$
$$H^+, Cl^- + K^+, OH^- \longrightarrow K^+, Cl^- + H_2O + 13{,}930 \text{ cal}$$
$$H^+, Cl^- + Li^+, OH^- \longrightarrow Li^+, Cl^- + H_2O + 13{,}700 \text{ cal}$$

The constant heat of neutralization reactions (approximately 13,780 cal) is the heat of formation of water by the union of a gram-ionic weight (g-ionic wt) of hydrogen ions with a gram-ionic weight of hydroxyl ions.

Titration of Acids and Bases · Since the neutralization of an acid with a base is represented by a definite chemical equation, it is evident that there is a definite relationship between the weight of acid and the weight of base reacting. Further, by the use of indicators it is possible to ascertain, when adding a base to an acid, the exact point at which sufficient base has been added to neutralize the acid. If the acid and base are in solution, and the solution of one of them is made up to contain a known weight of substance per unit volume of solution, then the *weight* of that substance needed to bring about the neutralization may be deter-

mined by measuring the *volume* of the solution necessary to bring the indicator to the neutral point. Such a solution, containing a known weight per unit volume, is called a *standard solution*, and the process of measuring the amount of it necessary to bring a reaction to completion is known as *titration*.

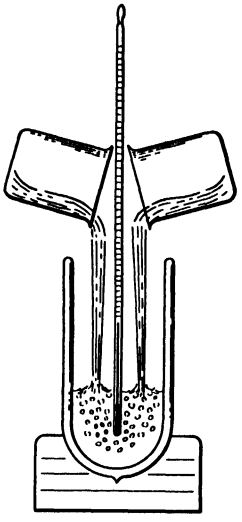


Fig. 14-1. Heat of Neutralization Pouring solutions of a strong acid and a strong base together into a Dewar-flask calorimeter

A titration is carried out with the aid of burettes (Fig. 14-2); these are tubes graduated in milliliters and furnished with a stopcock at one end. The one is filled to the zero mark with the acid solution, the other with the basic solution. A measured volume of the one solution is drawn off into a small beaker, a few drops of an appropriate indicator are added, and the second solution is run in with constant stirring until the indicator just turns color. If the concentration of the second solution is accurately known, then the weight of substance in the volume required for neutralization is known. The reaction indicated in the equation $NaOH + HCl \longrightarrow NaCl + H_2O$ (and similar ones) is perfectly definite, and, knowing the weight of an acid employed, we can calculate the weight of the base required for its neutralization and also the weight of the salt formed.

Normal Solutions · Although a standard solution may be of any convenient concentration, depending upon the character of the solutions being investigated, a particularly useful concentration for neutralization reactions is that of the normal solution. A normal solution of an acid contains, in 1 liter of solution, 1 g-ionic wt of replaceable hydrogen ions. A normal solution of a base contains 1 g-ionic wt (1.008 + 16.000 = 17.008 g) of replaceable hydroxyl ions. Solutions of half this concentration are said to be half-normal (0.5 N); of one tenth this concentration, tenth-normal (0.1 N); etc. The advantage of using these solutions is that equal volumes of acid and base solutions of the same normality will exactly neutralize each other.

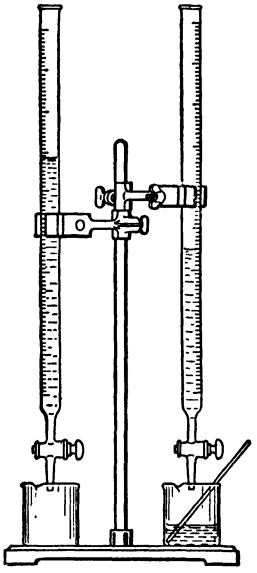


Fig. 14-2. Titration

In order to prepare a normal solution of a monobasic acid such as hydrochloric acid, it is evident that one must have present in each liter of the solution 1 g-mol. wt of the acid, since this amount would contain

1.008 g of hydrogen. Thus, a normal solution of hydrochloric acid will contain 36.465 g of hydrogen chloride (1.008 g H + 35.457 g Cl). With dibasic acids, on the other hand, 1 liter of the normal solution will contain only half the gram-molecular weight of the acid, since each molecule contains two hydrogen atoms. The same general principles hold in the preparation of a normal basic solution, which contains 17.008 g of the OH^- ion per liter.

Such solutions greatly simplify calculations, for it is evident that 1 liter of a normal solution of any acid will neutralize 1 molar weight of any monoacid base; 10 ml will neutralize $\frac{1}{100}$ of its molar weight. If, in neutralizing a solution of lye (NaOH) of unknown concentration, 20 ml of normal acid is required, the solution of lye contains $\frac{20}{1000} \times 40.005 = 0.8001$ g of sodium hydroxide.

In a normal solution of a strong acid like hydrochloric there is present a greater concentration of hydrogen ions than there is in a normal solution of a *weak* acid like acetic. However, the concentration of *potential* hydrogen ions is the same in each solution. Consequently the *same* amount of base is required to neutralize equal quantities of the two normal solutions. As rapidly as the hydrogen ions actually present in a solution of a weak acid enter into combination, other hydrogen ions are formed by the ionization of the weak acid.

Use of Normality · The use of normality to calculate the concentrations of solutions is demonstrated in the following problems. In many such calculations the relationship

Volume of solution A × normality of solution A = volume of solution B × normality of solution B,

or
$$V_A \times N_A = V_B \times N_B,$$

is used. For titrations involving acids and bases the relationship is expressed as

Volume of acid × normality of acid = volume of base × normality of base.

Examples. 1. Calculate the normality of a base 20 ml of which will neutralize 30 ml of 0.2 N acid.

$$V_A = 30 \text{ ml}; \qquad V_B = 20 \text{ ml};$$
$$N_A = 0.2; \qquad N_B = x.$$
$$30 \times 0.2 = 20 \times x;$$
$$x = \frac{30 \times 0.2}{20} = 0.3\ N.$$

2. How many milliliters of 0.2 N acid can be made from 400 ml of 0.5 N acid?

$$V_1 = 400 \text{ ml}; \qquad V_2 = x \text{ ml};$$
$$N_1 = 0.5; \qquad N_2 = 0.2.$$
$$400 \times 0.5 = 0.2 \times x;$$
$$x = \frac{400 \times 0.5}{0.2} = 1000 \text{ ml}.$$

Salts · It should be carefully noted that in a reaction of neutralization the removal of equivalent quantities of H^+ and OH^- ions through the formation of neutral water leaves in solution equivalent quantities of the (positive) cations of the base and (negative) anions of the acid. If this solution is concentrated by evaporation, these ions build neutral

crystals of solids called *salts. Salts, then, are, in general, electrically neutral compounds composed of cations of bases and anions of acids.*

Salts may be formed in a number of reactions other than those of neutralization. For example, they are formed by the action of acids on metals or on oxides:

$$Zn + 2\,H^+, SO_4^{--} \longrightarrow Zn^{++}, SO_4^{--} + H_2$$
$$Mg^{++}, O^{--} + 2(H^+, Cl^-) \longrightarrow Mg^{++}, 2\,Cl^- + H_2O$$

Varieties of Salts · From this description one might expect each acid to form as many salts as there are hydroxides or metals. This is not true, however, because some of the expected salts are too unstable to be prepared. Still the number of salts is very large. Among all these salts it is convenient to recognize three general types.

1. **Normal salts.** Salts such as those just described are called normal salts. *A normal salt is a compound built up wholly of the cations of any base and the anions of any acid.* In a formula it may be thought of as derived from an acid by replacing all its hydrogen by an equivalent metal, thus: NaCl, $ZnSO_4$.

General Properties of Normal Salts · Since there is no one ion characteristic of normal salts, there are no properties which they all have in common. In solubility they range between wide limits, some dissolving to an extent of less than a milligram per liter, and others dissolving in much less than their own weight of water. In degree of ionization the salts are found to be much more nearly the same than is the case with either acids or bases. In a general way it may be said that *they are nearly all strongly ionized.* The color of a salt is due sometimes to the anion and sometimes to the cation out of which the salt is built. When both are colorless (as is true with the majority of both acids and bases), the salt is likely to be colorless. When either has a marked color, the salts are all apt to share it in some degree. Thus, copper salts are usually some shade of blue or green, while the salts of the reddish chromic acid are usually yellow or orange.

2. **Acid salts.** With solutions of acids having more than one replaceable hydrogen atom (polyhydric) we may add such a quantity of a base as is equivalent to only 1 equivalent weight (or 2) of hydrogen:

$$Na^+, OH^- + 2\,H^+, SO_4^{--} \longrightarrow Na^+, H^+, SO_4^{--} + H_2O$$
$$K^+, OH^- + 3\,H^+, PO_4^{---} \longrightarrow K^+, 2\,H^+, PO_4^{---} + H_2O$$

The positive and negative ions remaining in solution then build crystals that may be represented by such formulas as $KHSO_4$ and KH_2PO_4. In solution the crystals give again all three ions. Such salts are called acid salts. *An acid salt is a salt composed of both metallic and hydrogen cations,*

together with the anions of an acid. It may be thought of as derived from an acid by the replacement of only a part of the available hydrogen by a metal. It is to be expected that in solution an acid salt gives the ions both of an acid and of a normal salt. Acid salts may also be formed in the way indicated in the equation

$$2\,K^+, SO_4^{--} + 2\,H^+, SO_4^{--} \longrightarrow 2(K^+, H^+, SO_4^{--})$$

3. **Basic salts.** The reaction of a polyhydroxyl base with a monohydrogen acid in proper proportion leads to the formation of a *basic* salt:

$$Pb^{++}, 2\,OH^- + H^+, NO_3^- \longrightarrow Pb^{++}, OH^-, NO_3^- + H_2O$$
$$Bi^{+++}, 3\,OH^- + H^+, NO_3^- \longrightarrow Bi^{+++}, 2\,OH^-, NO_3^- + H_2O$$

A basic salt is a salt composed of metallic cations, together with both hydroxyl anions of a base and anions of an acid. It will be seen that in solution a basic salt gives the ions both of a base and of a normal salt.

The Hydronium Ion **(H_3O^+)** · So far the hydrogen ion, formed by the ionization of an acid, has been indicated by the symbol H^+:

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

Now H^+ is a hydrogen atom that has lost its one valence electron and is the same as a proton, or nucleus, of a hydrogen atom. In volume it is much smaller than a hydrogen atom, and its electric charge is very intense. It is not likely that it would wander at large in a solution, and there are many reasons for believing that it forms a rather loose attachment to a water molecule:

$$H_2O + H^+ \rightleftarrows H^+(H_2O), \text{ or } H_3O^+$$

The resulting ion, H_3O^+, is called the *hydronium* ion. The ionization of any acid is really a reaction with water:

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^- \text{ (a strong acid, complete)}$$
$$HC_2H_3O_2 + H_2O \rightleftarrows H_3O^+ + C_2H_3O_2^- \text{ (a weak acid, incomplete)}$$

The heat evolved in dissolving hydrogen chloride in water or in diluting a concentrated solution of a strong acid is in large part due to the reaction with water. As a rule, not much is gained by substituting the symbol H_3O^+ for that of the simple ion H^+, and we shall do so merely in cases where it throws light on a reaction. For example, it is sometimes helpful to compare the two reactions

$$H_2O + H^+ \longrightarrow H_3O^+ \quad \text{and} \quad NH_3 + H^+ \longrightarrow NH_4^+$$

Brönsted Theory of Acids and Bases · While the definition of acids in terms of the hydrogen ion (properly the hydronium ion) and of bases in terms of the

hydroxyl ion is satisfactory for water solutions, it is evident that it is incomplete when applied to solutions in other solvents. For example, it has been demonstrated that a solution of hydrogen chloride in benzene, where there is no ionization, changes the color of indicators and exhibits certain catalytic effects in the same manner as solutions of hydrogen chloride in water, where hydronium ions are present. Further, sodium acetate, dissolved in liquid acetic acid, shows the properties of a base, although no hydroxyl ions are present. Consideration of these facts led the Danish chemist Brönsted and others to a new point of view about acids and bases and a definition free from ambiguity. Brönsted defined an acid as *any substance which by its own ionization or in a reaction can furnish a proton.* The substance resulting from the loss of the proton is a base:

$$\text{Acid} \rightleftarrows \text{base} + \text{H}^+$$

According to this definition, the term *acid* includes not only molecules, such as HCl, H_2SO_4, and H_3PO_4, but a great many ions, as shown below.

Acid		base	+ proton
H_3O^+	$\rightleftarrows$	H_2O	+ H^+
HCl	$\rightleftarrows$	Cl^-	+ H^+
HSO_4^-	$\rightleftarrows$	SO_4^{--}	+ H^+

Similarly bases include neutral molecules and a variety of ions of which hydroxyl is an outstanding example:

Base	+ proton		acid
NH_3	+ H^+	$\rightleftarrows$	NH_4^+
OH^-	+ H^+	$\rightleftarrows$	H_2O
$C_2H_3O_2^-$	+ H^+	$\rightleftarrows$	$HC_2H_3O_2$

Actually no great concentration of free protons ever exists at any one time, and no acid surrenders its proton unless there is a base present to receive the proton. Hence all acid-base reactions involve two acids and two bases:

Acid_1	+ base_2	$\rightleftarrows$	acid_2	+ base_1
HCl	+ H_2O	$\rightleftarrows$	H_3O^+	+ Cl^-
HNO_3	+ NH_3	$\rightleftarrows$	NH_4^+	+ NO_3^-
H_3O^+	+ OH^-	$\rightleftarrows$	H_2O	+ H_2O

Such reactions are proton-transfer reactions. The last equation represents what we have previously called a neutralization reaction. It is seen to be only one special type of acid-base reaction, but is of special significance because water is so frequently used as the medium for carrying out chemical reactions.

While the Brönsted theory is extremely useful in many connections, especially in the study of nonaqueous solutions, it does not in reality change the picture presented by the theory of ionization to any great extent. All acids in water yield protons (or rather hydronium ions), and all bases hydroxyl ions; so any measurement of the concentration of these ions is a true measure of the strength of an acid or a base.

Another definition of acids and bases is given in the discussion of the Lewis theory, on page 347.

QUESTIONS

1. Give definitions of the following: (*a*) *acid;* (*b*) *base;* (*c*) *neutralization;* (*d*) *indicator;* (*e*) *normal solution;* (*f*) *standard solution;* (*g*) *titration;* (*h*) *end point;* (*i*) *acid salt;* (*j*) *normal salt;* (*k*) *ionic equation;* (*l*) *hydronium ion;* (*m*) *dibasic acid.*

2. How can you account for the following facts?

a. A water solution of (1) hydrogen chloride (HCl), a covalent compound, has properties of a strong acid; (2) acetic acid ($HC_2H_3O_2$) has weak-acid properties; (3) wood alcohol (CH_3OH) is neutral.

b. A water solution of (1) sodium hydroxide (NaOH) has strong basic properties; (2) ammonium hydroxide (NH_4OH) has weak basic properties; (3) grain alcohol (C_2H_5OH) is neutral.

c. In the neutralization of hydrochloric acid with sodium hydroxide the sodium and chloride ions do not take part in the reaction.

d. Acids have a sour taste.

e. Acids neutralize bases.

f. Some acids will not dissolve copper.

3. Distinguish between (*a*) a hydrogen atom and a hydrogen molecule; (*b*) a hydrogen atom and a hydrogen ion; (*c*) a hydrogen ion and a hydronium ion.

4. What reactions other than the reaction of neutralization can be used to form salts?

5. Write equations showing the action of an acid on (*a*) a metal; (*b*) an oxide; (*c*) a hydroxide; (*d*) a peroxide; (*e*) a carbonate.

6. Write equations showing the complete neutralization of each of the three bases sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$), and aluminum hydroxide ($Al(OH)_3$), by each of the three acids hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4).

7. What salts are formed by the action of (*a*) 1 mole of sodium hydroxide (NaOH) on 1 mole of sulfuric acid (H_2SO_4)? (*b*) 1 mole of calcium hydroxide ($Ca(OH)_2$) on 1 mole of hydrochloric acid (HCl)? (*c*) 1 mole of calcium hydroxide ($Ca(OH)_2$) on 1 mole of phosphoric acid (H_3PO_4)? (*d*) 1 mole of calcium hydroxide ($Ca(OH)_2$) on 2 moles of phosphoric acid (H_3PO_4)?

8. Write equations to show the substances that are formed in the action of water on (*a*) carbon dioxide (CO_2); (*b*) sulfur dioxide (SO_2); (*c*) phosphoric oxide (P_4O_{10}); (*d*) sodium oxide (Na_2O); (*e*) calcium oxide (CaO); (*f*) aluminum oxide (Al_2O_3); (*g*) magnesium oxide (MgO); (*h*) ammonia (NH_3).

PROBLEMS

1. Calculate the number of grams of each of the following compounds required to make 1000 ml of a 1 *N* solution: (*a*) sodium hydroxide (NaOH); (*b*) hydrogen chloride (HCl); (*c*) sulfuric acid (H_2SO_4); (*d*) barium hydroxide ($Ba(OH)_2$); (*e*) nitric acid (HNO_3); (*f*) acetic acid ($HC_2H_3O_2$); (*g*) phosphoric acid (H_3PO_4); (*h*) ammonium hydroxide (NH_4OH).

2. Calculate the weight of each of the following compounds required to prepare 250 ml of the solution indicated: (*a*) 1 *N* HCl; (*b*) 0.1 *N* H_2SO_4; (*c*) 1 *N* $HC_2H_3O_2$ (acetic acid); (*d*) 0.1 *N* NaOH.

3. Twenty-five milliliters of a solution of acetic acid is exactly neutralized by 20 ml of a 0.1 *N* $Ca(OH)_2$ solution. What is the normality of the acetic acid solution?

4. A solution was found, on analysis, to contain 3.7 g of $Ca(OH)_2$ in 200 ml of solution. (*a*) What is the molarity of the solution? (*b*) What is the normality of the solution?

5. Twenty-eight milliliters of a normal solution of sodium hydroxide just neutralized 20 ml of a solution of sulfuric acid. Calculate the strength of the acid solution in terms of the weight of H_2SO_4 in 1 liter of solution.

6. Forty milliliters of a normal solution of sodium hydroxide was required to neutralize 12 ml of a solution of sulfuric acid. What volume of the latter is required to prepare 1 liter of 1 *N* H_2SO_4?

7. How many milliliters of 0.1 *N* HCl are necessary to neutralize (*a*) 50 ml of 0.25 *N* NaOH? (*b*) 20 ml of 0.1 *N* $Ba(OH)_2$?

8. How many milliliters of 0.1 *N* HCl are required to neutralize 5 g of solid NaOH?

9. (*a*) How many milliliters of 0.1 normal HCl solution can be made from 25 ml of 0.25 *N* HCl? (*b*) How much water must be added?

10. Twenty-five milliliters of 0.1 *N* NaOH is added to 25 ml of 0.25 *N* HCl. (*a*) Is the resulting solution acidic or basic? (*b*) Calculate the concentration of the acid in the mixture. (*c*) What weight of salt is formed?

11. How many milliliters of a 96 per cent solution of sulfuric acid of density 1.84 are required to make 1000 ml of 0.5 *N* sulfuric acid?

12. Twenty milliliters of 1 *N* HCl is mixed with 20 ml of 1 *N* NaOH. Calculate the temperature rise, assuming that the specific heat of the salt solution formed is the same as that of pure water.

13. Twenty milliliters of vinegar was titrated with 0.5 *N* NaOH. It required 32 ml of the base to neutralize exactly the acetic acid in the vinegar. What was the composition of the vinegar in per cent acetic acid? (Assume a density of 1.0 for the solution.)

CHAPTER 15

CHLORINE AND HYDROCHLORIC ACID; THE OXIDATION STATE

In the last chapter brief reference was made to the fact that sodium chloride is a source of chlorine and chlorine compounds. In this chapter we wish to study the properties of chlorine and of one of its most important compounds, hydrochloric acid.

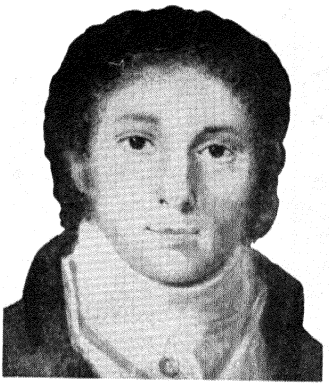


Fig. 15-1. Karl Wilhelm Scheele (1742–1787) · A Swedish chemist and one of the greatest experimenters of all times He discovered oxygen, ammonia, and hydrochloric acid independently of Priestley He also discovered chlorine, as well as the very poisonous gases arsine and hydrocyanic acid Among the organic compounds first prepared by Scheele are glycerin, milk sugar, lactic acid, gallic acid, citric acid, oxalic acid, and tartaric acid



Fig. 15-2. Sir Humphry Davy (1778–1829) · Appointed director of the Royal Institution of London when only twenty-two years of age Trained Michael Faraday as his assistant The first to isolate the metals sodium and potassium and to prove that chlorine is an element The inventor of the miner's safety lamp. (Reproduced from a painting by Sir Thomas Lawrence, by permission of the Royal Society, London)

Chlorine

History and Occurrence of Chlorine · The element chlorine was first isolated by Scheele (Fig. 15-1) in 1774. Because of its activity, it does not occur free in nature. Scheele obtained it by liberating it from hydrochloric acid by the action of manganese dioxide, a method of preparation

which is still used. For years the element was regarded as a compound of hydrochloric acid with oxygen until, in 1810, the English chemist Davy (Fig. 15-2) proved its elementary character, and because of its color named it *chlorine*, from a Greek word meaning "greenish yellow."

The Vorce Cell for the Production of Chlorine · In obtaining chlorine (and sodium hydroxide) by electrolysis of a salt solution (p. 232), chlorine

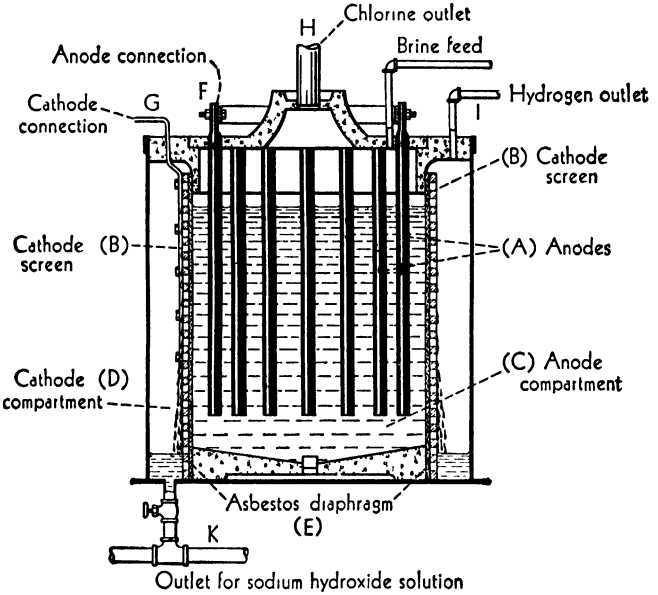


Fig. 15-3. The Vorce Cell for Producing Chlorine The salt brine is placed in a large cylindrical container and renewed from time to time through the brine feed. A number of graphite anodes, *A*, are dipped into the brine. The cathode of wire screening, *B*, surrounds the group of anodes in the form of a hollow cylinder, and is separated from the electrolyte by an asbestos diaphragm, *E*, to prevent mechanical stirring of the liquid. Hydrogen is evolved at the cathode and escapes through the hydrogen outlet, *I*. Chlorine is evolved at the anode surfaces, collects under the domelike top, and escapes through the chlorine outlet, *H*. The sodium hydroxide formed in the electrolysis is drawn off at the bottom, *K*, of the cell

evolved at the anode must be prevented from acting on the sodium hydroxide formed at the cathode. Several types of cells are in use in the United States for the production of chlorine, each designated by the name of its inventor. In the Vorce cell (Fig. 15-3) this is done by separating the anode and cathode compartments by a porous diaphragm. Under ordinary conditions each cell produces about 72 lb of sodium hydroxide and 64 lb of chlorine every twenty-four hours. The hydrogen evolved in the process is used in preparing hydrochloric acid and ammonia. The chlorine is used directly for bleaching, or is pumped into strong steel con-

tainers ranging in size from small flasks to tank cars. Sodium hydroxide is recovered from the cathode compartment.

The chief item of cost in the process is the generation of electrical energy, so that factories for the production of chlorine are likely to be located at points where hydroelectric power can be used to advantage, as at Niagara Falls.

Laboratory Preparation of Chlorine · On a small scale in the laboratory, chlorine is prepared by the oxidation of chloride ions with an oxidizing agent in the presence of hydrogen ions. For example, manganese dioxide (MnO_2) may be treated with hydrochloric acid:

$$MnO_2 + 4\ HCl \longrightarrow MnCl_2 + 2\ H_2O + Cl_2 \qquad (1)$$

If allowance is made for the fact that hydrochloric acid and manganese chloride are electrolytes, equation (1) may be rewritten as follows:

$$MnO_2 + 4\ H^+ + 4\ Cl^- \longrightarrow Mn^{++} + 2\ Cl^- + 2\ H_2O + Cl_2 \qquad (2)$$

It is seen that two of the chloride ions from the four molecules of hydrochloric acid do not take part in the reaction. An equation showing only those substances that do take part is

$$MnO_2 + 4\ H^+ + 2\ Cl^- \longrightarrow Mn^{++} + 2\ H_2O + Cl_2 \qquad (3)$$

The manganese is reduced, dropping from an electrovalence of + 4 to + 2, while the two chlorine ions are oxidized, increasing in electrovalence from − 1 to zero.

There is great advantage in writing ionic equations of this sort whenever possible. They are simpler, show more directly what the real reaction is, and are not loaded with ions which appear among both the reactants and the products and which do not take part in the reaction. The essential part of the reaction of equation (1) is shown by equation (3). If one uses sodium chloride as the source of chloride ions and sulfuric acid as the source of hydrogen ions, the same essential reaction as in equation (1) occurs, although this conclusion might not be obvious from the molecular equation (4):

$$MnO_2 + 2\ NaCl + 2\ H_2SO_4 \longrightarrow MnSO_4 + 2\ H_2O + Cl_2 + Na_2SO_4 \qquad (4)$$

The essential part of the reaction, however, can again be written

$$MnO_2 + 4\ H^+ + 2\ Cl^- \longrightarrow Mn^{++} + 2\ H_2O + Cl_2 \qquad (3)$$

and it is clear that the reaction is the same, regardless of the source of hydrogen ions and chloride ions. The sodium ions and sulfate ions play no part in the reaction.

Experimental details. The manganese dioxide and hydrochloric acid are placed in the flask, *A* (Fig. 15-4), and thoroughly mixed. A gentle heat is then

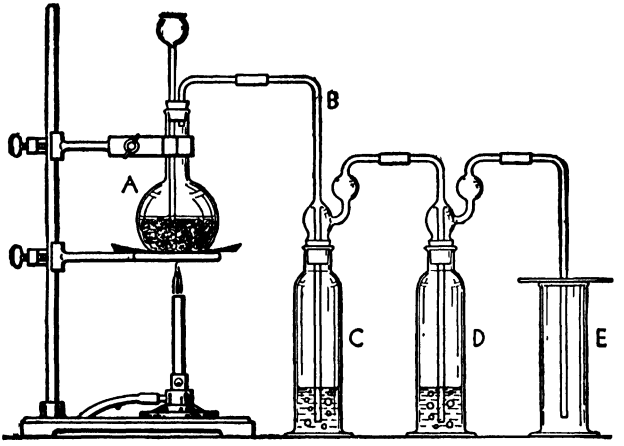


Fig. 15-4. Diagram of Apparatus Used in the Laboratory for Preparing Chlorine by the Action of Hydrochloric Acid on Manganese Dioxide

applied to the flask. Chlorine is evolved and, escaping through the tube, *B*, bubbles through the water in the bottle *C* (which dissolves any hydrochloric acid carried over with it) and finally through some sulfuric acid in the bottle *D* (which removes any moisture present). Since the gas is fairly soluble in water, it is collected by displacing the air in the cylinder, *E*. Because of the poisonous character of chlorine, its preparation should be carried out cautiously in a well-ventilated hood.

Balancing the Equations for Oxidation-Reduction Reactions • When oxidizing agents other than manganese dioxide are used to oxidize chloride ions, some difficulty may be experienced in writing balanced equations for the reactions that occur. A useful plan to follow is to write, first, the electronic partial equations, showing the gain or loss of electrons, and then adjust the number of molecules or ions involved so that the number of electrons gained by the oxidizing agent is equal to the number lost by the reducing agent. In writing the electronic partial equations for reactions which take place in solution, water and its ions (the hydrogen ion and the hydroxyl ion) may be used at will as reagents, since they are always present. Of course, as with any reaction, the products of the reaction must be known before the equation can be written.

Example. When hydrochloric acid is added to potassium permanganate, chlorine is formed.

Step 1. The products of the reaction are the manganous ion (Mn^{++}), chlorine, and perhaps water; the reactants are the permanganate ion (MnO_4^-), the hydrogen ion, and the chloride ion.

Step 2. The electronic partial equation for the oxidation is simply

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \qquad (5)$$

The skeleton of the electronic partial equation for the reduction is

$$MnO_4^- \longrightarrow Mn^{++} \qquad (6)$$

This is not balanced with respect to the atoms present, since no oxygen-containing substance appears on the right. To correct this, add hydrogen ions to the left and water to the right, and balance materially:

$$MnO_4^- + 8\,H^+ \longrightarrow Mn^{++} + 4\,H_2O \qquad (7)$$

This does not balance electrically, since the total charge on the left is 7+ and on the right 2+. It will balance electrically if five electrons are entered as reactants:

$$5\,e^- + MnO_4^- + 8\,H^+ \longrightarrow Mn^{++} + 4\,H_2O \qquad (8)$$

Step 3. The balanced electronic partial equations must now be made to correspond with each other. Since two electrons appear as products and five as reactants, it is evident that a total of ten electrons (least common multiple) must be transferred, or

$$10\,Cl^- \longrightarrow 5\,Cl_2 + 10\,e^- \qquad (9)$$

$$10\,e^- + 2\,MnO_4^- + 16\,H^+ \longrightarrow 2\,Mn^{++} + 8\,H_2O \qquad (10)$$

and, adding,

$$10\,Cl^- + 2\,MnO_4^- + 16\,H^+ \longrightarrow 5\,Cl_2 + 2\,Mn^{++} + 8\,H_2O \qquad (11)$$

Equation (11) is the balanced ionic equation for the oxidation of chloride ions by permanganate ions in an acid solution.

Another method for balancing equations for oxidation-reduction reactions is given on page 257, after *oxidation state* has been discussed.

Properties of Chlorine · Chlorine is a greenish-yellow gas and possesses a peculiar suffocating odor. It is 2.49 times as heavy as air, and under ordinary conditions 1 volume of water dissolves about 2.5 volumes of the gas. At ordinary temperatures (18°) it is liquefied by a pressure of 10.5 atm. In commercial containers (iron cylinders or tank cars) it is largely in the liquid state. Liquid chlorine is yellowish in color, boils at −34.6° under atmospheric pressure, and freezes at −101.6°. Its critical temperature is 144°. When inhaled in small quantities, chlorine produces the symptoms of a hard cold, and in larger quantities has serious and even fatal effects.

Chemical Properties · At ordinary temperatures chlorine is one of the most active of all the elements. The compounds formed by its union with any other element are called *chlorides*.

1. **Action upon other elements.** Nearly all the metals combine directly with chlorine, especially when heated or powdered. A strip of copper foil,

heated to redness and immediately dropped into chlorine, burns with incandescence. Sodium burns brilliantly when heated strongly in moist chlorine. Gold and silver are quickly tarnished by the gas, and even platinum is readily attacked by it.

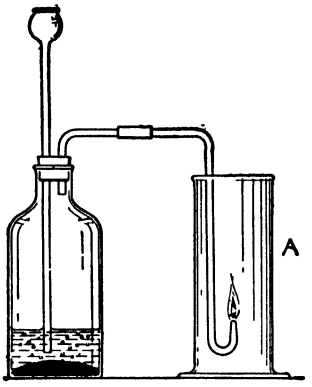


Fig. 15-5. Hydrogen Burning in an Atmosphere of Chlorine

Chlorine has likewise a strong affinity for most of the nonmetals. Phosphorus, sulfur, antimony, and arsenic burn in a current of the gas.

Chlorine unites readily with hydrogen, forming hydrogen chloride. A jet of hydrogen burning in the air continues to burn when introduced into a jar, *A*, of chlorine, giving a somewhat luminous flame (Fig. 15-5). A mixture of the two gases explodes violently either when heated or when exposed to bright sunlight.

2. **Action upon compounds of hydrogen.** Not only will chlorine combine directly with free hydrogen, but it will remove hydrogen from some of its compounds. Thus, when chlorine is passed into an aqueous solution of hydrogen sulfide, sulfur is precipitated and hydrochloric acid formed, as expressed in the following equation:

$$H_2S + Cl_2 \longrightarrow 2\,HCl + S\downarrow \qquad (12)$$

With ammonia the action is similar:

$$2\,NH_3 + 3\,Cl_2 \longrightarrow 6\,HCl + N_2 \qquad (13)$$

Under certain conditions the reaction with ammonia yields a very explosive, oily liquid known as nitrogen trichloride (NCl_3). The strong affinity of chlorine for hydrogen is very strikingly shown by its action upon turpentine($C_{10}H_{16}$). When a strip of paper moistened with warm turpentine is placed in a jar of the gas, the chlorine unites with the hydrogen of the turpentine with evolution of light, forming hydrogen chloride, while a black deposit of carbon remains.

3. **Action upon water.** At ordinary temperature and pressure one volume of water dissolves a little over two volumes of chlorine, and the solution is called *chlorine water*. Slightly above the freezing point of water a solid hydrate separates, which has the composition $Cl_2 \cdot 8\,H_2O$. When warmed, this compound dissociates into its constituents; and it was by taking advantage of these properties that Faraday, in 1823, first liquefied chlorine (Fig. 11-10, p. 175).

Chlorine in solution slowly reacts with the water to form small concentrations of hydrochloric acid and a compound called hypochlorous acid (HClO), but an equilibrium is soon reached:

$$Cl_2 + H_2O \rightleftarrows HCl + HClO \qquad (14)$$

The hypochlorous acid decomposes into hydrochloric acid and oxygen, slowly in diffused light but rapidly in bright sunlight; and the final result is a solution of hydrogen chloride and evolved oxygen:

$$2\,HClO \longrightarrow 2\,HCl + O_2\uparrow \qquad (15)$$

The decomposition of water through the action of chlorine is also greatly increased in the presence of some substance which combines with the oxygen as fast as it is set free. Consequently a solution of chlorine in water is a good oxidizing agent.

Experiment. The effect of sunlight in increasing the action of chlorine upon water may be shown in the following way. If a long tube of rather large diameter is filled with a saturated solution of chlorine in water and inverted in a vessel of the same solution (Fig. 15-6), and the apparatus is placed in bright sunlight, bubbles of gas will soon be seen to rise through the solution and collect in the tube. An examination of this gas will show that it is oxygen.

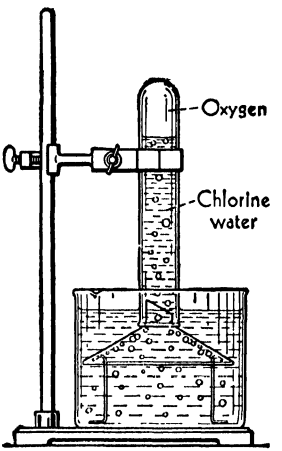


Fig. 15-6. Action of Chlorine on Water in Bright Sunlight

4. **Action as a germicide.** Chlorine has marked *germicidal properties*, and both the free element and the compounds from which it is easily liberated are used as disinfectants and antiseptics. For this reason free chlorine is widely used in the purification of city water supplies.

5. **Action of moist chlorine on colored materials; bleaching.** Chlorine water is a powerful bleaching agent. Strips of highly colored cloth, when moistened with water and placed in jars of chlorine, often lose their color. The presence of water is essential to the change, as may be shown by placing strips of the dry cloth in chlorine from which the moisture has been removed by bubbling it through sulfuric acid (Fig. 15-4). Under these conditions the color of the cloth remains unchanged or nearly so.

The bleaching action of chlorine is in reality due to the oxidizing action of hypochlorous acid, as explained in No. 3 (p. 248); the oxygen reacts with the color substance of the cloth to form colorless compounds. Chlorine has no bleaching action on substances that are not easily oxidized.

such as carbon, and so does not affect printer's ink. It should not be used for bleaching certain substances, such as silk, since it injures the fabric.

Bleaching is an important process in connection with many industries: Thus, the various kinds of fabrics woven from vegetable fibers, such as flax and cotton, are always more or less colored, and bleaching is necessary if a white fabric is desired. This was formerly accomplished by spreading the cloth on plots of grass and exposing it to air and sunlight, but the process was very slow. The same results are now obtained in a short time by the use of chlorine.

The nascent state. The student may well ask, "Why does the oxygen from hypochlorous acid have a rapid bleaching effect, while free oxygen itself bleaches colors very slowly?" The simplest answer is that at the instant oxygen is set free from a compound, it consists of free *atoms*, whereas oxygen gas is made up of oxygen *molecules*. The free atoms are more active than the molecules, as is evident from the fact that work must be done to part the molecules into atoms. The parted atoms then have additional energy and on this account enter into reactions more rapidly than molecules. To distinguish between the energetic uncombined atoms and the molecules, we say that the atoms at the instant of liberation from compounds are in the *nascent state*. The word *nascent* means "newborn."

Uses · Chlorine is one of the most important industrial reagents. Its production in 1950 in the United States amounted to about 6000 tons daily. Most of this is used in bleaching fabrics or the wood pulp from which paper is made. It is also used in the purification of water and in making *bleaching powder* and such compounds as chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), polyvinyl chloride, and various antiseptics and disinfectants and other organic compounds.

Hydrogen Chloride and Hydrochloric Acid

With hydrogen, chlorine forms the simple gaseous compound *hydrogen chloride* (HCl). This gas is very soluble in water, and the resulting solution is called *hydrochloric acid*. This distinction between the compound itself and its solution in water is desirable, though it is not always observed.

Preparation of Hydrogen Chloride and Hydrochloric Acid · Two general methods for preparing hydrogen chloride will be described. To prepare hydrochloric acid, it is only necessary to dissolve hydrogen chloride gas in water.

1. **By the direct combination of hydrogen and chlorine.** These two gases readily combine, forming hydrogen chloride (p. 248). Since both the hydrogen and the chlorine are obtained in quantities in the electrolysis of a solution of sodium chloride, this method is used to a limited extent in the preparation of hydrogen chloride on an industrial scale.

2. By the action of concentrated sulfuric acid upon chlorides of metals. Because of its low cost sodium chloride is always used for this purpose. The reaction takes place in two steps. The first,

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow \qquad (16)$$

takes place upon bringing the salt and sulfuric acid together at ordinary temperatures. The second requires heating and is as follows:

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl\uparrow \qquad (17)$$

By combining the two equations the following is obtained:

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl\uparrow \qquad (18)$$

It will be observed that in this reaction sodium sulfate is formed along with hydrogen chloride. Since there is a considerable use for sodium sulfate, this method of preparation has an advantage in that both compounds formed are of value. The first reaction is a convenient one for the preparation of hydrogen chloride in the laboratory.

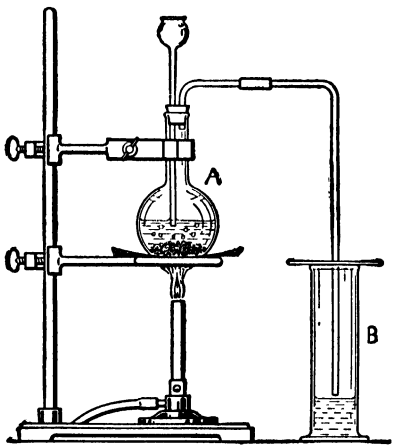


Fig. 15-7. The Preparation of a Solution of Hydrogen Chloride

Laboratory preparation. Sodium chloride is placed in the flask, *A* (Fig. 15-7), which is fitted with a funnel tube and an exit tube; sulfuric acid of the proper concentration is added, and the flask is gently warmed. Hydrogen chloride is evolved, since it is insoluble in *concentrated sulfuric acid*, and is collected by displacement of air, as in the preparation of chlorine. To prepare a solution of the gas, the end of the exit tube is fixed just above the level of some water contained in a cylinder, *B*. Since the gas is extremely soluble in water, it is absorbed as fast as it escapes from the tube. Care must be taken not to have the end of the exit tube dip below the surface of the water, since the solubility of the gas is so great that the water would suck back into the generating flask and cause trouble.

If the sulfuric acid is added, not to the solid sodium chloride but to an aqueous solution of the salt, there is no very marked action. The hydrogen chloride formed is very soluble in water and so does not escape from the solution; consequently a state of equilibrium is soon reached among the ions of the four substances represented in the equation.

Liberation of hydrogen chloride from its solution. The pure hydrogen chloride can easily be regained from its concentrated aqueous solution by the addition of sulfuric acid, which diminishes the solubility of the hydrogen chloride. This is a very convenient method for obtaining pure gaseous hydrogen chloride

when a limited supply of it is desired in the laboratory. The concentrated solution is placed in *A* (Fig. 15-8), and the flask is connected with the bottle, *B*, which contains sulfuric acid for drying the gas. This bottle is fitted with stopper and tubes, as shown in the diagram. The glass tube leading from the bottle, *B*, to the bottom of the cylinder, *E*, passes through a perforated cardboard or glass plate, *C*, which rests lightly on the top of the cylinder. Sulfuric acid is now added, drop by drop, from the separatory funnel, *D*, to the concentrated solution in *A*. The hydrogen chloride is rapidly evolved and is collected in the cylinder, *E*, as shown in the figure.

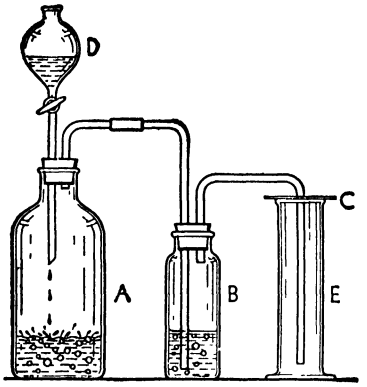


Fig. 15-8. Liberating Hydrogen Chloride from Its Solution

By-products · In the preparation of any given substance it usually happens that other compounds are formed. These are called *by-products*. Thus sodium sulfate is a by-product in the manufacture of hydrochloric acid (p. 251). It is evident that the cost of the manufacture of any substance can be decreased to the extent to which the by-products can be utilized. Indeed, the demand for the by-product may become so great that it really comes to be the main product. The success of a process often depends upon the value of its by-products.

Properties of Hydrogen Chloride · Hydrogen chloride, a colorless gas, is 1.26 times as heavy as air. When inhaled, it has an irritating and suffocating effect. At 0° it is condensed to the liquid state by a pressure of 28 atm. This liquid is colorless, boils at −85°, and solidifies at −111°. *It does not conduct electricity, has no action upon metals, and in general is inactive.* Hydrogen chloride is very soluble in water, 1 volume of the latter under standard conditions dissolving 506 volumes of the gas. The density of its aqueous solutions increases with the concentration of the gas, as is shown in the following table, which gives the percentage *by weight* of hydrogen chloride present in solutions of various densities at 15°:

DENSITY OF SOLUTIONS OF HYDROCHLORIC ACID					
PER CENT OF HCl	DENSITY	PER CENT OF HCl	DENSITY	PER CENT OF HCl	DENSITY
5.69	1.0284	20.04	1.1006	35.02	1.1779
10.17	1.0507	25.06	1.1265	40.09	1.2013
15.22	1.0761	30.00	1.1526	43.40	1.2134

A solution of hydrogen chloride in water, containing 20.24 per cent of the gas, has a constant boiling point (110°) at a pressure of 760 mm

(p. 194). Solutions more concentrated lose hydrogen chloride on boiling, while more dilute solutions lose water, until the concentration above is reached, when they boil with unchanged concentration.

Solubility of hydrogen chloride. The extreme solubility of hydrogen chloride in water may be shown as follows: A perfectly dry flask, *A* (Fig. 15-9), is filled with hydrogen chloride. This flask is connected, by means of a glass tube, with a similar flask, *B*, which is nearly filled with water, as shown in the figure. The end of the tube opening into flask *A* is drawn out to a rather fine jet. By blowing into the tube, *C*, a few drops of water are forced into *A*. Some of the hydrogen chloride at once dissolves, which diminishes the pressure inside the flask. The water then flows continuously from *B* into *A*, until practically all the hydrogen chloride is absorbed. It is evident that the connections must be airtight.

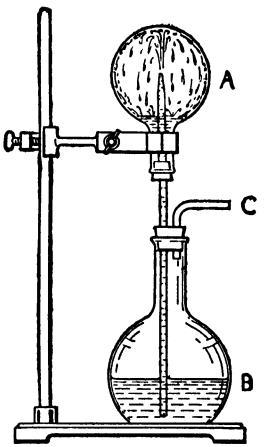


Fig. 15-9. Apparatus for Showing the Extreme Solubility of Hydrogen Chloride in Water

Properties of Hydrochloric Acid · When pure materials are used, the solution of hydrogen chloride in water (hydrochloric acid) is a colorless liquid. The commercial acid, often colored yellow by impurities, is frequently called *muriatic acid*. While hydrogen chloride itself has but little chemical activity, *its aqueous solution*, because it contains hydrogen ions (p. 233), shows all the properties characteristic of acids (sour taste, action on indicators, reaction with metals and their hydroxides and oxides; see pages 233–234). Its chief uses are those based on these acid properties.

Chlorides · The salts of hydrochloric acid, in which the hydrogen of the acid has been replaced by a metal, are known as *chlorides*, and constitute an extremely important group of compounds. Some of them, as sodium chloride and potassium chloride, are found in nature. A number of the metals, including copper, mercury, and tin, combine with different percentages of chlorine, and thus form two chlorides. Nearly all the chlorides of the metals are solids; and, with the exception of those of silver, mercury (mercurous), and lead, the chlorides of all the common metals are soluble in water.

Some of the more important chlorides are the following: *sodium chloride* (*common salt*) ($NaCl$); *potassium chloride* (KCl); *mercurous chloride* (*calomel*) (Hg_2Cl_2); *mercuric chloride* (*corrosive sublimate*) ($HgCl_2$); *ferric chloride* ($FeCl_3$); *barium chloride* ($BaCl_2$); *calcium chloride* ($CaCl_2$); *zinc chloride* ($ZnCl_2$).

Oxidation State, or Oxidation Number

Definition of Oxidation State · In Chapter 13 we gave a general definition of oxidation and reduction, namely, *oxidation* is the removal of electrons from an atom or group of atoms; *reduction* is the addition of electrons to an atom or group of atoms. In the reaction between zinc and hydrochloric acid the essential reaction is

$$\overset{0}{Zn} + 2\overset{+1}{H} \longrightarrow \overset{+2}{Zn} + \overset{0}{H_2} \qquad (19)$$

and consists in the transfer of two electrons from the zinc atom to the two hydrogen ions. We may therefore describe the reaction as a change in electrovalence of the zinc atom from 0 to + 2 and of each hydrogen ion from + 1 to 0. The zinc is oxidized, since electrons are removed from it; and the hydrogen ions are reduced, since electrons are added to them. The oxidation state of Zn^{++} is greater than that of Zn, and the oxidation state of H_2 is less than that of $2\ H^+$.

A similar case is that of the oxidation of chloride ions by permanganate ions in the presence of hydrogen ions:

$$10\ Cl^- + 2\ MnO_4^- + 16\ H^+ \longrightarrow 5\ Cl_2 + 2\ Mn^{++} + 8\ H_2O \qquad (11)$$

which, as the electronic partial equations (5) and (8), on page 247, show, results from the loss of electrons from chloride ions, and the gain of electrons by permanganate ions in the presence of hydrogen ions:

$$2\ Cl^- \longrightarrow \overset{0}{Cl_2} + 2\ e^- \qquad (5)$$

$$5\ e^- + MnO_4^- + 8\ H^+ \longrightarrow Mn^{++} + 4\ H_2O \qquad (8)$$

The oxidation state of $2Cl^-$ is less than that of Cl_2, since electrons are removed in going from the one to the other, and the oxidation state of manganese in the permanganate ion (MnO_4^-) is greater than that of manganese in the manganous ion (Mn^{++}), since electrons are gained in this transformation. In the case of the zinc and hydrogen ion the change in oxidation state could be equally well expressed as a change in electrovalence; this is also true for the oxidation of chloride ions. In the case of manganese in the permanganate ion, however, it is not proper to speak of an electrovalence of manganese, since the manganese atom and oxygen atoms are probably combined with covalent bonds. Nevertheless, it is useful to retain for this case also the numbering system used for electrovalences, and assign to the manganese in the permanganate ion an oxidation state of + 7, so that the gain of five electrons will produce the ion Mn^{++} (electrovalence, + 2), just as would have been the case if the bonds in the permanganate ion had been electrovalent bonds. *The oxidation*

state of an element in a compound or ion is defined as the charge which an atom of that element would have if the substance contained only ions, regardless of whether the bonds in the substance are really electrovalent or not.

Rules for Calculating the Oxidation State · The assignment of oxidation states to the elements in a compound may be made by observing certain rules:

1. *The algebraic sum* (the sum taking account of positive and negative signs) *of the oxidation states of all the atoms in a compound must equal zero*, just as is the case for electrovalences in electrovalent compounds. If the substance being examined is an ion rather than a compound, then the algebraic sum of the oxidation states of the atoms in the ion must equal the charge on the ion.

2. *Hydrogen has an oxidation state of + 1 and oxygen an oxidation state of − 2* when they are present in compounds. Exceptions to this are that hydrogen has an oxidation state of − 1 in hydrides of active metals, and oxygen has an oxidation state of − 1 in peroxides, and of + 2 in its compound with fluorine.

3. *The oxidation state of a free element (that is, one not combined with another element) is zero.*

The application of these rules gives to simple ions an oxidation state equal in magnitude and sign to the charge on the ion; that is, for ions, the oxidation state is equal to the electrovalence. For compounds containing covalent bonds, the oxidation state of an element may be determined by applying rules such as those above.

The oxidation state of an element may vary from compound to compound. The common oxidation states of several elements are given in the table on page 256.

Examples of the Calculation of Oxidation State · **Example 1.** Calculate the oxidation state of sulfur in sulfur dioxide (SO_2).

If the oxidation state of oxygen is − 2, the total oxidation state for two oxygen atoms must be − 4. Hence the oxidation state of sulfur in sulfur dioxide must be + 4 in order that Rule 1 may be satisfied.

$$2\,O = 2 \times (-2) = -4$$
$$S = \underline{+4}$$
$$0$$

Example 2. Calculate the oxidation state of sulfur in hydrogen sulfate (H_2SO_4).

The total oxidation state for 2 H is	$2\,H = 2 \times (+1) = +2$
The total oxidation state for 4 O is	$4\,O = 4 \times (-2) = -8$
Therefore the oxidation state of S in H_2SO_4 is	$S = \underline{+6}$
	0

TABLE OF OXIDATION STATES

ELEMENT	COMPOUND	OXIDATION STATE
Aluminum	All	+3
Bromine	Bromides	−1
Calcium	All	+2
Chlorine	Chlorides	−1
Chlorine	Chlorates	+5
Chromium	Chromic	+3
Chromium	Chromates	+6
Copper	Cupric	+2
Iron	Ferrous	+2
Iron	Ferric	+3
Manganese	Manganous	+2
Manganese	Permanganates	+7
Nitrogen	Nitrides	−3
Nitrogen	Nitrates	+5
Phosphorus	Phosphates	+5
Potassium	All	+1
Sodium	All	+1
Sulfur	Sulfides	−2
Sulfur	Sulfites	+4
Sulfur	Sulfates	+6

Example 3. Calculate the oxidation state of chlorine in potassium chlorate ($KClO_3$).

The electrovalence of potassium is +1; hence the oxidation state for 1 K is

$$K = +1$$

The total oxidation state for 3 O is $3\,O = 3 \times (-2) = -6$

Therefore the oxidation state of Cl in $KClO_3$ is $Cl = +5$

$$0$$

Example 4. Calculate the oxidation state of manganese in the permanganate ion (MnO_4^-).

The total oxidation state for 4 O is $4\,O = 4 \times (-2) = -8$

Therefore the oxidation state of Mn must be $Mn = +7$

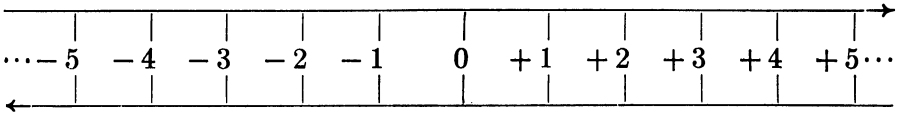
in order that the charge on the ion may be −1 (Rule 1). -1

Usefulness of the Concept of Oxidation State · The value of the concept of oxidation state must be determined by its usefulness to chemists, since it is admittedly an arbitrary system and in many cases is not directly related to the type of bond in the compound. A knowledge of the oxidation state of an element in its compounds enables us to classify data concerning those compounds. Thus, chlorine compounds in which chlorine has an oxidation state of −1 have quite different properties from those of compounds of chlorine in its +5 state, and the two groups may be discussed separately. Further, a knowledge of the oxidation state provides an easy means for finding out which elements are oxidized and which

reduced in oxidation-reduction reactions, and for balancing oxidation-reduction equations.

Oxidation and Reduction in Terms of Oxidation State · Oxidation is an algebraic increase in oxidation state; reduction is an algebraic decrease in oxidation state. This is illustrated in the following diagram:

Oxidation is toward more positive oxidation states.



Reduction is toward more negative oxidation states.

The change in oxidation state indicates the elements oxidized or reduced.

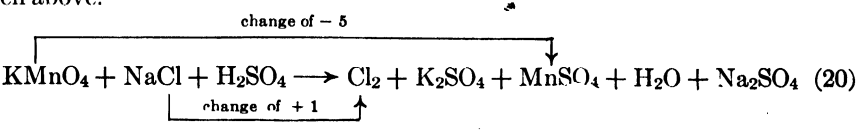
Example. When potassium permanganate is treated with sodium chloride and sulfuric acid, chlorine, potassium sulfate, manganous sulfate, water, and sodium sulfate are formed:

$$\left.\begin{matrix}KMnO_4\\NaCl\\H_2SO_4\end{matrix}\right\} \longrightarrow \left\{\begin{matrix}Cl_2\\K_2SO_4\\MnSO_4\\H_2O\\Na_2SO_4\end{matrix}\right.$$

The calculation of the oxidation states of each element in the reactants and products shows that the oxidation states of all the elements remain unchanged except those of chlorine and manganese. In the case of chlorine the oxidation state goes from − 1 (in NaCl) to 0 (in Cl_2), and in the case of manganese the oxidation state goes from + 7 (in $KMnO_4$) to + 2 (in $MnSO_4$). Thus, the chlorine is oxidized and the manganese reduced.

Balancing Equations by the Oxidation-State Method · Having discovered what element is oxidized and what reduced, we may write and balance the equation for an oxidation-reduction reaction. The rule is that *the total change in the oxidation state of one element must be equal and opposite to the total change in the oxidation state of another.* This corresponds to the statement that for any oxidation there must be an equal amount of reduction; and to the statement that the number of electrons gained in the reduction must equal the number lost in the oxidation reaction. The same rule is followed in balancing electronic partial equations.

Example. Balance the equation for the reaction indicated in the example given above.



The changes in oxidation state of manganese and chlorine are indicated. The total change for chlorine must be + 5 to equal the total change for manganese; this will require five chlorine atoms, or 5 NaCl. However, chlorine appears as Cl_2 in the products, so that 5 NaCl could form only $2\frac{1}{2}$ Cl_2. In order to balance the equation, therefore, we must multiply by 2, so that we have 10 NaCl and 5 Cl_2. This makes a total oxidation-state change for chlorine of + 10; so we must also multiply $KMnO_4$ by 2 to give 2 $KMnO_4 \longrightarrow 2\ MnSO_4$, with a total oxidation-state change of − 10. With these figures the equation is

$$2\ KMnO_4 + 10\ NaCl + H_2SO_4 \longrightarrow 5\ Cl_2 + K_2SO_4 + 2\ MnSO_4 + H_2O + Na_2SO_4 \quad (21)$$

The remainder of the equation may now be balanced by inspection. There are eight oxygen atoms in the 2 $KMnO_4$, which evidently appear as H_2O; so there must be 8 H_2O in the products. To supply the sixteen hydrogen atoms (in 8 H_2O) we need 8 H_2SO_4. When three of the eight sulfate ions have been used for $K_2SO_4 + 2\ MnSO_4$, the other five appear in 5 Na_2SO_4, which includes the ten sodium atoms from 10 NaCl, and the equation is balanced.

$$2\ KMnO_4 + 10\ NaCl + 8\ H_2SO_4 \longrightarrow 5\ Cl_2 + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ Na_2SO_4 \quad (22)$$

Balancing Oxidation-Reduction Equations of the Ionic Type · It has been pointed out (p. 245) that there is a great advantage in writing equations in ionic form where ions are involved. For example, the equation just shown is equally— in fact, more nearly— correct when written

$$2\ MnO_4^- + 10\ Cl^- + 16\ H^+ \longrightarrow 5\ Cl_2 + 2\ Mn^{++} + 8\ H_2O,$$

since the K^+, Na^+, and SO_4^{--} ions take no actual part in the reaction. The question now arises, "Can I write this equation directly without going through the molecular form?" The answer is Yes, and the process is less complicated than the other, provided we keep track of the charges on the ions. Following are the steps:

1. **Write down the correct symbols or formulas for the reactants and products** (without regard to water or its ions). For this reaction we would have

$$MnO_4^- + Cl^- \longrightarrow Mn^{++} + Cl_2$$

This much must be known, namely, that the MnO_4^- ion, when it acts as an oxidizing agent in acid solution, yields Mn^{++}, and that the chloride ion, when oxidized, yields Cl_2. From this point the equation may be balanced by a systematic procedure.

2. **Check oxidation states.** Manganese is + 7 in MnO_4^-, + 2 in Mn^{++}; chlorine is − 1 in Cl^-, 0 in Cl_2; a change of − 5 for manganese, + 1 for chlorine.

3. **Balance oxidation against reduction.** This requires a ratio of 5 Cl^- to 1 MnO_4^-, or, since the chlorine appears as Cl_2, a ratio of 10 Cl^- to 2 MnO_4^-. So we write

$$2\ MnO_4^- + 10\ Cl^- \longrightarrow 2\ Mn^{++} + 5\ Cl_2$$

4. **Balance charges.** An ionic equation must balance electrically as well as chemically. Since this reaction takes place in aqueous solution, we may assume that water and its ions are involved. Note that, as the equation now stands, there are 12− charges on the left and 4+ charges on the right. We can balance charges either by adding 16 H^+ on the left or 16 OH^- on the right. Since the reaction takes place in the presence of acid, the former is preferred, and the equation becomes

$$2\ MnO_4^- + 10\ Cl^- + 16\ H^+ \longrightarrow 2\ Mn^{++} + 5\ Cl_2$$

5. **Complete the material balance.** A final examination now shows an excess of 16 hydrogen atoms and 8 oxygen atoms on the left. Presumably 8 molecules of water are formed, and the equation is complete:

$$2\ MnO_4^- + 10\ Cl^- + 16\ H^+ \longrightarrow 2\ Mn^{++} + 5\ Cl_2 + 8\ H_2O$$

Various Methods of Balancing Oxidation-Reduction Equations · There are thus several methods of balancing oxidation-reduction equations, including the method of electronic partial equations, described on page 246, as well as the change of oxidation-state method as applied both to nonionic and ionic equations. The student should practice all of the methods to develop skill and confidence in this art.

QUESTIONS

1. Define the terms (*a*) *by-products;* (*b*) *electronic partial equations;* (*c*) *oxidation state, or oxidation number;* (*d*) *oxidation;* (*e*) *reduction.*

2. (*a*) What simple, fundamental change is necessary to convert chloride ions to chlorine molecules? (*b*) Give two different methods of doing this.

3. (*a*) Contrast the properties of chloride ions and chlorine molecules. (*b*) Do you find a similar large difference between the properties of sodium ions and sodium atoms? (*c*) How do you account for these differences?

4. Name two properties either of which would enable you to distinguish chlorine from all the other gases studied in the preceding chapters.

5. Mention two discoveries made by Scheele.

6. Write the equations for the reactions that take place in the preparation of each of the following substances from sodium chloride: (*a*) chlorine; (*b*) hydrogen chloride.

7. (*a*) Why are some gases collected over water and others not? (*b*) What gases so far studied are collected over water?

8. What property has chlorine that makes it effective in the purification of water supplies?

9. Write complete and balanced equations for the reaction of chlorine with (*a*) hydrogen; (*b*) water; (*c*) copper; (*d*) antimony; (*e*) turpentine; (*f*) sodium; (*g*) hydrogen sulfide.

10. Why does a covalent compound like hydrogen chloride, when dissolved in water, form a solution which conducts the electric current?

11. Calculate the oxidation state of (*a*) manganese in MnO_2; (*b*) potassium in K_2O; (*c*) sulfur in H_2S; (*d*) sulfur in SO_2; (*e*) sulfur in H_2SO_3; (*f*) nitrogen in NH_3; (*g*) nitrogen in HNO_3; (*h*) manganese in the MnO_4^- ion; (*i*) sulfur in the SO_3^{--} ion; (*j*) carbon in H_2CO_3.

12. (*a*) Indicate the oxidation state of each element in the following equations:

$$2\,Cu + O_2 \longrightarrow 2\,CuO$$
$$Cu + Cl_2 \longrightarrow CuCl_2$$

(*b*) What do you find that these equations have in common? (*c*) Is oxygen necessary for an oxidation process?

13. Write balanced ionic equations for the following reactions for the preparation of chlorine. Balance each equation by the oxidation-state method.

a. $MnO_2 + HCl \longrightarrow$

b. $MnO_4^- + Cl^- + H^+ \longrightarrow$

c. $MnO_2 + Cl^- + H^+ \longrightarrow$

d. $CrO_4^{--} + Cl^- + H^+ \longrightarrow Cr^{+++} + Cl_2 + H_2O$

e. $ClO_3^- + Cl^- + H^+ \longrightarrow Cl_2 + H_2O$

14. In the following unbalanced equations both reactants and products are shown. In each case write the electronic partial equation and the final ionic equation.

a. $Zn + H^+ \longrightarrow Zn^{++} + H_2$

b. $CrO_4^{--} + H^+ + Br^- \longrightarrow Cr^{+++} + Br_2 + H_2O$

c. $NO_3^- + H^+ + S^{--} \longrightarrow NO + H_2O + S$

d. $Fe^{+++} + Sn^{++} \longrightarrow Fe^{++} + Sn^{++++}$

15. In the following equations both reactants and products are shown; balance the equations by use of the oxidation-state method:

a. $H_2S + HNO_3 \longrightarrow S + NO + H_2O$

b. $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

c. $MnO_2 + NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + Cl_2 + H_2O$

d. $SO_2 + KMnO_4 + H_2O \longrightarrow K_2SO_4 + MnSO_4 + H_2SO_4$

PROBLEMS

1. One kilogram of sodium chloride, dissolved in water, will yield, on electrolysis, (*a*) what volume of chlorine gas? (*b*) what volume of hydrogen gas? (*c*) what weight of sodium hydroxide?

2. (*a*) How many grams of sodium chloride are required to produce 1500 ml of hydrogen chloride measured under standard conditions? (*b*) If all this hydrogen

chloride is dissolved in enough water to make 1000 ml of solution, what is the molar concentration of the resulting solution?

3. A student wished to prepare chlorine by the action of hydrochloric acid on manganese dioxide. He used 50 ml of hydrochloric acid, density 1.2013. (*a*) What weight of manganese dioxide was required to liberate the chlorine? (*b*) What volume of chlorine (measured under standard conditions) was liberated?

4. In normal times approximately 3200 tons of chlorine is prepared daily in the United States by the electrolysis of sodium chloride. (*a*) What weight of sodium chloride is required daily in its preparation? (Assume that 5 per cent of the chlorine is lost.) (*b*) Calculate the weight of the sodium hydroxide formed. (*c*) Calculate the weight of hydrogen liberated in the process.

5. Calculate the weight (*a*) of sodium chloride and (*b*) of sulfuric acid required to prepare 100 kg of hydrochloric acid of density 1.1779.

6. What weight of lime (calcium oxide, CaO) must be used to neutralize a solution containing 182.5 g of hydrogen chloride?

7. What weight of silver nitrate must be used in order to prepare 40 g of silver chloride?

8. What volume of hydrogen chloride, measured at 740 mm and 25°, must be passed into 20 ml of 0.5 *N* NaOH in order to make a neutral solution of sodium chloride?

9. What weight of sodium hydroxide will react with the hydrochloric acid obtainable from 10 kg of sodium chloride?

10. A Vorce cell will produce 64 lb of chlorine in 24 hr. Assuming that you are operating a chlorine plant composed of 50 such cells, and that all the chlorine in the sodium chloride used is liberated, calculate the weight of sodium chloride required weekly for operating the plant on a 24-hour basis.

11. Fifty milliliters of 0.5 molar calcium hydroxide ($Ca(OH)_2$) is added to 75 ml of 0.5 molar hydrochloric acid. (*a*) Is the resulting solution acidic or basic? (*b*) Calculate the molar concentration of the hydrogen or hydroxyl ion which is in excess.

This tendency is most marked with fluorine and least with iodine. Elements which tend to attract and hold electrons are called electronegative elements. Fluorine is the most electronegative of all the elements as measured by the force of attraction between it and electrons.

These elements, with the exception of fluorine, form a series of compounds in which some or all of the seven valence electrons are removed or shared. They can, therefore, exist in several oxidation states, as illustrated by the various acids of chlorine, HCl, HClO, $HClO_2$, $HClO_3$, and $HClO_4$, in which chlorine shows oxidation states of -1, $+1$, $+3$, $+5$, and $+7$. The higher oxidation states are more common with the larger atoms, since these lose electrons more readily. Fluorine is found only as a negative ion, while the other elements display positive oxidation states as well. Collectively, these elements are called the *halogens* (salt-formers).

History and Occurrence of the Halogens · Since these elements all form ions so readily and since most of their compounds are soluble, they are found in considerable quantities in sea water. None of them exists in the free state in nature.

Fluorine occurs most abundantly in nature in the minerals fluorite, cryolite, and fluorapatite. *Fluorite*, or fluorspar, is calcium fluoride (CaF_2). It is found in many places, and in large deposits, especially in Illinois and Kentucky. *Cryolite*, a fluoride of sodium and aluminum (Na_3AlF_6), is found in Greenland and Iceland. *Fluorapatite* is the most abundant of the three and consists of calcium fluoride combined with calcium phosphate, as represented in the formula $CaF_2 \cdot 3\ Ca_3(PO_4)_2$. Traces of compounds of fluorine are also found in sea water, in many minerals, in bones, and in the enamel of the teeth. In some localities compounds of fluorine occur in the drinking water, and this is reported to have a beneficial effect in the prevention of tooth decay. While the compounds of fluorine have long been known, all efforts to liberate the element failed until the year 1886, when the French chemist Moissan (Fig. 16-2) finally succeeded in isolating it and made an extended study of its properties and of its chemical activity toward other elements.



Fig. 16-2. Tablet Erected by the Associates and Friends of Moissan in His Laboratory in Paris in 1906 on the Twentieth Anniversary of the Isolation of Fluorine

Bromine is one of the few elements that are liquid under ordinary conditions. It occurs in nature as the bromide ion in solutions of certain salts, principally those of sodium, potassium, calcium, and magnesium. These salts are known as *bromides*. Bromides are present in sea water. Small percentages of bromides are found in the famous potash deposits at Stassfurt, Germany (see Stassfurt salts). They also occur in the waters of many springs and in the brine pumped from deep wells, especially in Michigan, mixed with much larger quantities of sodium chloride.

History. It was from salt brines that the German chemist Liebig first isolated bromine. He concluded, however, that the red liquid which he obtained was a compound of chlorine and iodine. A few months later (1826) the French chemist Ballard again obtained the substance from similar liquors. He rightly considered it to be an elementary substance, and, because of its disagreeable odor, named it *bromine*, from a word meaning "stench."

Iodine compounds are present in sea water, but in such small percentages that it is difficult even to detect their presence. Certain seaweeds absorb the iodine from the water, and it was from ashes obtained by burning seaweeds (kelp) that the French chemist Courtois, in 1812, first isolated the element. Because of the violet color of its vapor he named it *iodine*, from a Greek word meaning "violet-colored." Iodine is also found in some marine animals, such as sponges, oysters, and some fishes. It occurs, as sodium iodate, in the deposits of Chile saltpeter (sodium nitrate). It is interesting to note that the adult human body contains about 50 mg of iodine, approximately one third of which is in compounds in the thyroid gland; and it is generally believed that lack of iodine is the cause of certain forms of the rather common disease of this gland known as *goiter*.

Astatine, a fifth element belonging to this family, was discovered, in 1940, as a result of nuclear reactions in which bismuth was bombarded by alpha particles (see Chapter 21). The name *astatine* comes from a Greek word meaning "unstable." The element is radioactive, changing in a short time into other elements. Since its existence is only transient, it probably does not occur in nature. It will, therefore, not be discussed further here.

Preparation of the Free Halogens · The preparation of any one of these elements, in the free state, involves the removal of an electron from each ion and the union of the atoms to form diatomic molecules. For example:

$$2 : \underset{\text{ion}}{\ddot{\underset{\cdot\cdot}{F}}}\ :^- \longrightarrow : \underset{\text{molecule}}{\ddot{\underset{\cdot\cdot}{F}} : \ddot{\underset{\cdot\cdot}{F}}} : + 2\,e^-$$

or

$$2\,F^- \longrightarrow F_2 + 2\,e^- \qquad 2\,Br^- \longrightarrow Br_2 + 2\,e^-$$

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \qquad 2\,I^- \longrightarrow I_2 + 2\,e^-$$

The method of preparation chosen in each case and the compound used to provide the ions depend on the availability of the compound and on the relative strength with which the electrons are held. Three general methods are available:

1. Electrolysis of a solution or of a melted salt.
2. Displacement of one element by one of the others.
3. Oxidation of the ions Cl^-, Br^-, I^-, by means of oxidizing agents in acid solution.

Fluorine · Because of the strength with which the electrons are held in the fluorine ion, the only method by which fluorine may be prepared in satisfactory yield is that of electrolysis. This must be carried out in the absence of water because of the violence with which fluorine reacts with water. Moissan electrolyzed a solution of potassium hydrogen fluoride (KHF_2) dissolved in liquefied hydrogen fluoride (HF). More recent experiments have shown that fluorine can be readily prepared, in large quantities if desired, by the electrolysis (in a copper cell) of a *melted* potassium hydrogen fluoride ($KF \cdot 3\,HF$) with the use of pure graphite electrodes (Fig. 16-3).

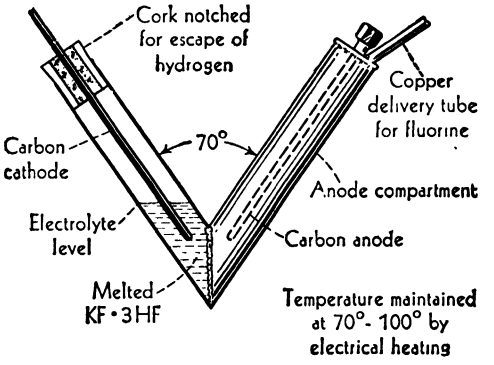


Fig. 16-3. Diagram of Apparatus for the Preparation of Fluorine

Chlorine · The methods used for the preparation of chlorine are described in Chapter 15. Both electrolytic methods and methods based on the use of oxidizing agents, such as MnO_2, are available.

Bromine · The general methods used in the preparation of chlorine may likewise be employed in liberating bromine from its compounds.

Laboratory Methods. In the laboratory, bromine is prepared by the action of oxidizing agents upon hydrogen bromide. It is convenient to generate the hydrogen bromide in the course of the reaction by using a mixture of sodium bromide and sulfuric acid. The oxidizing agent ordinarily used is manganese dioxide. The reaction is exactly like that used in the preparation of chlorine:

$$2\,NaBr + 2\,H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + Br_2\uparrow$$

The bromide and manganese dioxide are thoroughly mixed and are then put in the retort, *A* (Fig. 16-4), the end of which just touches the water in the flask, *B*.

The sulfuric acid is then added. When the retort is gently heated, the bromine is liberated, distills over, and collects under the water in the flask. The latter is kept cool by immersion in ice water in the beaker, *C*.

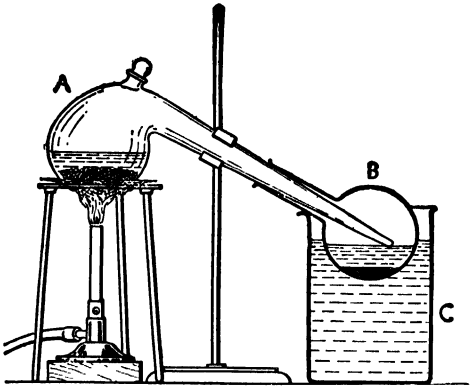


Fig. 16-4. The Laboratory Preparation of Bromine

Another method is based upon the fact that chlorine molecules will oxidize bromide ions (in solutions of bromides):

$$2\,NaBr + Cl_2 \longrightarrow 2\,NaCl + Br_2$$

or $$2\,Br^- + Cl_2 \longrightarrow 2\,Cl^- + Br_2$$

This reaction is often used as a test for the bromide ion. The test comprises adding chlorine water, which has a pale-green tinge, to the solution being tested. If the bromide ion is present, free bromine is formed. This can be detected by its reddish-brown color. The addition of chloroform or carbon disulfide, which serves to dissolve and thereby concentrate the bromine, makes the color easier to see.

Extraction of bromine from the sea. Until recently the great center for the production of bromine in the United States has been in the vicinity of Midland, Michigan, where the bromine was recovered from natural brines pumped from deep wells. Smaller amounts were obtained from brines of the Ohio River valley and a few other places. The Michigan brines contain about 25 per cent by weight of dissolved solids and about 1300 parts per million of bromine in the form of bromides. In 1924 about 2,000,000 lb of bromine was used in this country, and in 1950 about 116,500,000 lb. This sharp increase in demand resulted largely from the increasing use of bromine (as ethylene bromide, $C_2H_4Br_2$) along with tetraethyl lead in gasoline. It finally seemed desirable to call on the sea to yield up some of its enormous and inexhaustible supply of bromine. Deep sea water carries only 67 parts per million of bromine (as bromides), but, even so, there are about 600,000,000 lb per cubic mile of water.

In choosing a location for a recovery plant, it seemed necessary to find a site (on the beach) not too near the mouth of a river, so that the sea water would *not be diluted*; nor should the water be contaminated by organic matter. It was desirable to locate near a railroad; but railroad facilities are generally available near cities, and the coastal cities are invariably situated near the mouth of a river. All things considered, the small peninsula off Wilmington, North Carolina, separating the Atlantic Ocean from the Cape Fear River, seemed almost ideal for the purpose; and there a plant was built in 1934. The bromine was

made to react with ethylene to form ethylene dibromide. Initially the plant had a capacity of 13.5 tons of ethylene dibromide a day, and this was later increased. But the Wilmington plant was discontinued in 1945, and a still larger plant was built at Freeport, Texas, during World War II. In 1945 we were using annually 18,000,000 lb of ethylene dibromide and in 1950 about 30,000,000 lb.

In this modern plant for the recovery of bromine, the sea water is first made slightly acid by the addition of sulfuric and hydrochloric acids. It is then sprayed into a tower (the blowing-out tower in Fig. 16-5), where it comes into contact

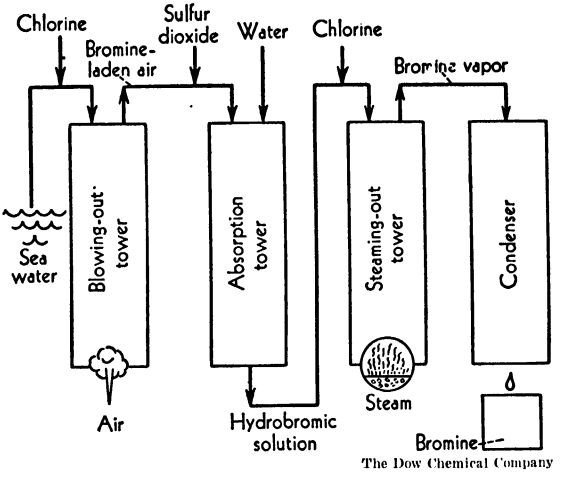


Fig. 16-5. Process for Producing Bromine from Sea Water

with chlorine gas. The liberated bromine is blown out with air, and an equivalent quantity of sulfur dioxide is introduced into the bromine-laden air, in the absorption tower. In the presence of water vapor the sulfur dioxide reduces the bromine vapors to hydrogen bromide and the chlorine to hydrogen chloride:

$$SO_2 + Br_2 + 2\,H_2O \longrightarrow H_2SO_4 + 2\,HBr$$
$$SO_2 + Cl_2 + 2\,H_2O \longrightarrow 2\,HCl + H_2SO_4$$

Thus the bromine is separated from the large volume of air and obtained in the form of a concentrated solution of hydrobromic acid. Chlorine gas is now added to this acid mixture to form free bromine again, and the bromine is steamed out and collected. The mixture of sulfuric and hydrochloric acids which remains is used in the first step of the process to increase the acidity of the sea water. The only raw materials, other than sea water, needed in this process are sulfur and chlorine.

Iodine · Iodine is set free from the iodides by the action of sulfuric acid and manganese dioxide. The reaction is similar to that which takes place in the liberation of chlorine from the chlorides and of bromine from the bromides.

$$2\,NaI + 2\,H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + I_2\uparrow$$

Chlorine has already been described (p. 247).

Bromine is a dark-red liquid whose density is 3.119. The liquid boils at 58.7° and solidifies at −7.2°, but even at ordinary temperatures it has a high vapor pressure and forms a reddish-brown vapor. The vapor has an offensive odor and is very irritating to the eyes and throat. One hundred volumes of water dissolves about 1 volume of liquid bromine at 20°. The solution is called *bromine water*. Bromine is readily soluble in carbon disulfide and carbon tetrachloride. The chemical behavior of bromine is very similar to that of chlorine, except that it is less active. It combines directly with many of the same elements with which chlorine unites, but with less energy. Bromine water is often used as an oxidizing agent.

Iodine is a purplish-black, shining solid which, when sublimed, crystallizes in brilliant plates belonging to the rhombic system. It has a density of 4.93, melts at 113.5°, and boils at 184.3°. The element has a strong, unpleasant odor, although not so disagreeable as that of chlorine or bromine. Even at ordinary temperatures it gives off a beautiful violet vapor, which increases as heat is applied. It is only slightly soluble in water—1 part in 3750 parts of water at 15°. It is very readily soluble in a solution of potassium iodide or of hydrogen iodide, forming a dark-brown liquid. It also dissolves in carbon disulfide, forming a violet-colored liquid.

Iodine is similar to chlorine and bromine in its chemical properties, but is less active. Both the latter elements liberate iodine from its ions in solution (by oxidation):

$$2\ I^- + Cl_2 \longrightarrow 2\ Cl^- + I_2$$
$$2\ I^- + Br_2 \longrightarrow 2\ Br^- + I_2$$

Like chlorine and bromine it combines directly with many of the metals, as well as with the nonmetals. In the presence of water it acts as a mild oxidizing agent.

The usual test for free iodine is made by adding a few drops of the solution to be tested to a starch solution. The appearance of a blue color is a very sensitive test for free iodine.

Crystal Lattice of Iodine · Fig. 16-7 shows the crystal lattice of iodine. One of the interesting features about this lattice is that the iodine exists in the lattice as a twin atom, or dumbbell molecule. It will be recalled that measurements of gas density show many *gases* to be made up of diatomic molecules, such as H_2, O_2,

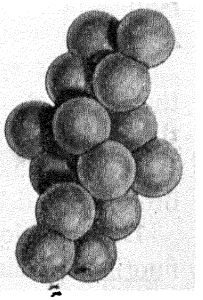


Fig. 16-7. Crystal Lattice of Iodine

N_2, and Cl_2. Here we have independent evidence, based on X-ray analysis, that iodine molecules are I_2 in the *solid* state.

Uses of the Free Elements · Large quantities of fluorine, which is now available commercially, are used in the preparation of fluorine-containing hydrocarbons, such as Freon, an excellent refrigerant (p. 177), and other products, including plastics, such as teflon. Such fluorinated compounds tend to be extremely inert and resistant to the action of solvents and corrosive chemical substances. Hydrogen fluoride (HF) is an important intermediate in the industrial processes in which high-octane gasoline and polystyrene plastics are manufactured.

The uses of chlorine have been discussed previously.

The demand for bromine has fluctuated greatly in recent years. Potassium and sodium bromides find use as medicinal agents, and silver bromide is used in photography. Today the chief use of bromine is in the preparation of ethylene dibromide, a constituent of "ethyl gasoline." It is also used in the manufacture of certain dyes and other organic compounds.

The chief use of iodine is in the manufacture of potassium and sodium iodides and of certain organic drugs and dyes. Silver iodide (AgI) is an important compound of iodine used in photography. The ordinary *tincture of iodine*, used largely as an antiseptic, is a solution of iodine and potassium iodide in alcohol; a colloidal dispersion of the element is also used for the same purpose. Iodine is likewise a valuable reagent in the laboratory.

Hydrogen Compounds of the Halogens

The preparation and properties of hydrogen chloride have already been discussed (pp. 250-253). It is of interest to compare the hydrogen compounds of fluorine, bromine, and iodine (HF, HBr, and HI) with hydrogen chloride and with one another.

Methods of Preparation · Two general methods were described for the preparation of hydrogen chloride, direct union of the elements and the action of concentrated sulfuric acid on the salt. If one uses these same methods in the attempt to prepare hydrogen fluoride, hydrogen bromide, and hydrogen iodide, characteristic differences are observed.

Direct union of the elements. Unless special precautions are taken, fluorine combines with hydrogen with explosive violence. Chlorine unites vigorously with hydrogen, and bromine somewhat less vigorously, while the reaction between iodine and hydrogen takes place only very slowly.

In practice only hydrogen chloride is made by direct union of the elements; the preparation of free fluorine is too difficult, and the reactions do not take place readily in the cases of bromine and iodine.

Action of sulfuric acid on a salt. This reaction, which is based on the displacement of a volatile acid by a nonvolatile one, may be used with success in preparing hydrogen fluoride or hydrogen chloride. In preparing hydrogen fluoride the naturally occurring fluorspar is used:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,HF\uparrow$$

This reaction is carried out in vessels of platinum or lead, and is the method commonly used in the preparation of the aqueous solutions of hydrogen fluoride, in which form hydrogen fluoride is ordinarily used. This is also the method used in preparing hydrogen chloride (p. 251).

One would naturally expect that hydrogen bromide could be prepared in the same general way as hydrogen fluoride and hydrogen chloride, namely, by the action of sulfuric acid upon a bromide such as NaBr or KBr:

$$2\,NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HBr\uparrow$$

This reaction does indeed take place; the hydrogen bromide is evolved in the form of a colorless gas which fumes strongly in the air. At the same time *some bromine* is liberated, as is indicated by the formation of a reddish vapor. The odor of sulfur dioxide can also be detected. This method, therefore, cannot be used for the preparation of pure anhydrous hydrogen bromide, although it may be adapted to the preparation of a dilute aqueous solution. The reason why pure hydrogen bromide cannot be prepared by this method is that the bromide ion, unlike the chloride ion, is oxidized by the sulfuric acid:

Oxidation:	$2\,Br^- \longrightarrow Br_2 + 2\,e^-$
Reduction:	$4\,H^+ + SO_4^{--} + 2\,e^- \longrightarrow SO_2 + 2\,H_2O$
Ionic equation:	$2\,Br^- + 4\,H^+ + SO_4^{--} \longrightarrow Br_2 + SO_2 + 2\,H_2O$
Molecular equation:	$2\,HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2\,H_2O$

Attempts to prepare hydrogen iodide by this method fail for the same reason as that given above. Any hydrogen iodide formed is immediately oxidized by the sulfuric acid.

Other methods. Pure hydrogen fluoride is best prepared by heating anhydrous potassium hydrogen fluoride in a platinum vessel:

$$KHF_2 \longrightarrow KF + HF\uparrow$$

The method usually employed in the preparation of hydrogen bromide consists in the action of water upon phosphorus tribromide. The latter

compound is a colorless liquid formed by the union of phosphorus and bromine, and has the formula PBr_3. Water acts upon this compound, with the formation of hydrogen bromide and phosphorous acid:

$$PBr_3 + 3\ H_2O \longrightarrow H_3PO_3 + 3\ HBr\uparrow$$

Experimental details. Some red phosphorus is put in a flask, *A* (Fig. 16-8), and enough water is added to cover it. By means of the stopcock, *E*, bromine is allowed to flow, drop by drop, from the funnel, *B*, into the flask. The phosphorus tribromide which forms in the flask then reacts with water. The U-tube, *C*, contains glass beads which have been moistened with water and rubbed in red phosphorus. Any bromine escaping action in the flask acts upon the phosphorus in the U-tube. The hydrogen bromide is collected in *D* by displacement of air. An aqueous solution of the gas is easily prepared.

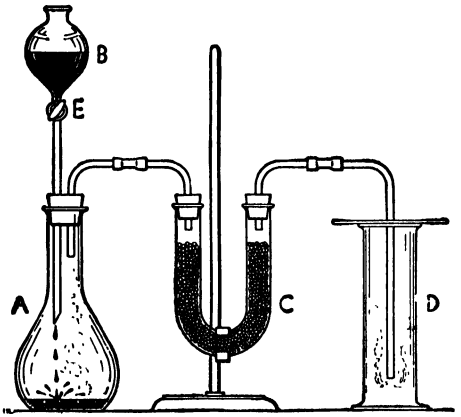


Fig. 16-8. The Preparation of Hydrogen Bromide

This general method could be used also to prepare HCl, since the compound PCl_3 is easily prepared and hydrolyzes readily. However, the action of sulfuric acid on salt is much more convenient.

The method generally employed for the preparation of hydrogen iodide is similar to that used for the preparation of hydrogen bromide and consists in the reaction between phosphorus tri-iodide and water:

$$PI_3 + 3\ H_2O \longrightarrow H_3PO_3 + 3\ HI\uparrow$$

The hydrogen iodide is evolved as a heavy, colorless gas and may be collected by the displacement of air. Hydrogen iodide may also be obtained by passing a mixture of gaseous hydrogen and iodine vapor over a heated catalyst. An aqueous solution of the gas can be prepared by passing hydrogen sulfide into water containing finely divided iodine in suspension:

$$H_2S + I_2 \longrightarrow 2\ HI + S\downarrow$$

When the oxidation-reduction reaction is complete, the precipitated sulfur is removed by filtration. Solutions of the gas can be prepared in this way up to 50 per cent strength. The freshly prepared solution is colorless, but soon turns brown, owing to the liberation of iodine by the oxygen of the air:

$$4\ HI + O_2 \rightleftarrows 2\ H_2O + 2\ I_2$$

Properties of the Hydrogen Compounds of the Halogens · **1. Stability.** The stability of the hydrogen compounds of the halogen elements decreases rapidly in the order HF, HCl, HBr, and HI. The relative stabilities of these compounds are indicated by comparison of the per cent dissociation at 1000°. These data are obtained by heating each compound, separately, in a sealed tube (Fig. 16-9), and determining the amount of free element present when equilibrium has been established (see Chapter 24).

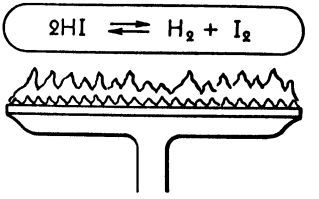


Fig. 16-9

PER CENT DISSOCIATION OF THE HYDROGEN HALIDES AT 1000°

HF	No dissociation observable
HCl	1.34×10^{-13} per cent (0.000000000000134 per cent)
HBr	0.144 per cent
HI	29.0 per cent

2. Reaction with water; the hydrohalogen acids. While HF, HCl, HBr, and HI are covalent compounds, aqueous solutions of them are acidic. This can best be accounted for as being the result of a reaction with water, in which hydronium ions (p. 239) are formed:

$$HF + H_2O \longrightarrow H_3O^+ + F^-$$
$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$
$$HBr + H_2O \longrightarrow H_3O^+ + Br^-$$
$$HI + H_2O \longrightarrow H_3O^+ + I^-$$

Aqueous solutions of these compounds are called hydrofluoric, hydrochloric, hydrobromic, and hydriodic acids. The equation for their ionization is usually written in the simpler form, showing the hydrogen ion, H^+ (see page 239).

The acid properties of solutions of hydrogen fluoride are masked somewhat by the tendency of the latter to form complex molecules—H_2F_2, H_6F_6, etc. For this reason hydrofluoric acid is a weak acid. The other acids, however, are relatively strong.

Hydrogen Fluoride and Hydrofluoric Acid · Vapor-density measurements indicate that the vapor of hydrogen fluoride is a mixture of molecules represented by the formulas HF and H_6F_6, but it is customary to use the simpler formula, HF. Hydrogen fluoride is a colorless liquid that boils at 19.4°. At low temperatures it forms a white solid melting at −83°. An aqueous solution containing 35 per cent HF is a constant-

boiling mixture (p. 194), boiling at 120° under standard pressure, and distills with unchanged concentration.

Pure hydrogen fluoride is a nonconductor of electricity and is neutral in reaction. When dissolved in water it ionizes as follows:

$$HF \rightleftarrows H^+ + F^-$$

The resulting solution is acid in character and is known as *hydrofluoric acid.* Ordinary commercial hydrofluoric acid contains about 50 per cent of hydrogen fluoride. Since this solution readily attacks glass, it is kept in bottles made of wax, paraffin-like materials, or certain plastics.

Hydrofluoric acid is a rather weak acid. It acts upon some of the metals, as well as upon their oxides and hydroxides, forming the corresponding salts. A single drop in contact with the skin produces a very painful wound, slow to heal. If inhaled, its vapor is very injurious.

A distinguishing property of hydrofluoric acid is its action upon glass. Ordinary glass consists principally of a mixture of sodium silicates and calcium silicates, together with an excess of silica (SiO_2). Hydrofluoric acid reacts with these silicates, forming solid fluorides of sodium and calcium, together with gaseous silicon tetrafluoride (SiF_4). The equations for these reactions are as follows:

$$Na_2SiO_3 + 6\ HF \longrightarrow 2NaF + SiF_4\uparrow + 3\ H_2O$$
$$CaSiO_3 + 6\ HF \longrightarrow CaF_2 + SiF_4\uparrow + 3\ H_2O$$
$$SiO_2 + 4\ HF \longrightarrow SiF_4\uparrow + 2\ H_2O$$

Advantage is taken of this property in marking thermometers and flasks, as well as in etching designs on glassware.

Etching glass. Etching with hydrofluoric acid is done in the following way: A piece of glass is covered with a thin coating of some wax, such as paraffin, by melting the wax on the glass and tilting the glass until it is completely covered with a thin film. After the wax hardens, the design is cut through it with a fine-pointed tool. The object so prepared is then exposed to the fumes of hydrofluoric acid. The acid attacks the glass wherever exposed, destroying its luster and leaving the design etched upon its surface.

Salts of Hydrofluoric Acid: the Fluorides · The most important salt of hydrofluoric acid is the well-known mineral *fluorite* (CaF_2), or calcium fluoride. The fluorides of most of the metals can be prepared by the usual method for preparing salts, namely, by the action of the acid upon the metals directly or upon their oxides or hydroxides. A number of the univalent metals form acid salts, such as potassium hydrogen fluoride (KHF_2).

Hydrogen Chloride and Hydrochloric Acid · The properties of this compound were described in a preceding chapter (see page 252).

Hydrogen Bromide and Hydrobromic Acid · Hydrogen bromide very strikingly resembles hydrogen chloride in its properties. It is a colorless, strongly fuming gas and may be condensed to a colorless liquid which boils at $-67°$. It is very soluble in water. Under standard conditions 1 volume of water dissolves 612 volumes of the gas. The resulting solution has a density of 1.5 and contains 88 per cent of the gas. An aqueous solution containing 48 per cent of hydrogen bromide boils at 126° under ordinary pressure and distills with unchanged concentration. Hydrogen bromide, like hydrogen chloride, has but little activity. When dissolved in water, however, it dissociates into the ions H^+ and Br^-, so that the solution is strongly acid and is known as *hydrobromic acid.* This acid is very similar to hydrochloric acid and reacts with metals and with their oxides and hydroxides, forming the corresponding bromides.

Salts of Hydrobromic Acid: the Bromides · The bromides are, in general, very similar to the chlorides in their properties, and are prepared by the same general methods. The bromides of the common metals are all soluble except silver bromide, mercurous bromide, and lead bromide.

Hydrogen Iodide and Hydriodic Acid · Hydrogen iodide resembles hydrogen chloride and hydrogen bromide in its physical properties, being a strongly fuming, colorless gas. It is easily condensed to a colorless liquid that boils at $-35.5°$ under a pressure of 4 atm. At 10° about 450 volumes of the gas dissolves in 1 volume of water. A solution containing 57 per cent of hydrogen iodide boils at 127° and distills with unchanged concentration.

Owing to the ease with which the gas is decomposed into its elements, it acts in many respects like hydrogen, being a strong reducing agent. When dissolved in water, it ionizes as follows:

$$HI \rightleftarrows H^+ + I^-$$

This solution has strong acid properties due to the hydrogen ions present, and is known as *hydriodic acid.*

Salts of Hydriodic Acid: the Iodides · The iodides are similar to the corresponding chlorides and bromides but are not so stable toward heat. They are all solids and, with the exception of the iodides of silver, mercury, and lead, are soluble in water.

Oxygen Compounds of the Halogens

Introduction · Not only do the halogen elements exist in an oxidation state of − 1 in such compounds as we have just been discussing, but, with the exception of fluorine, they form oxygen acids and salts, in which their oxidation states may be + 1, + 3, + 5, and + 7, as is shown in the following table:

OXYGEN COMPOUNDS OF THE HALOGENS		
HYDRIDES	OXIDES	OXYGEN ACIDS
HF	F_2O, F_2O_2	——
HCl	Cl_2O, Cl_2O_6, Cl_2O_7, ClO_2	HClO, $HClO_2$, $HClO_3$, $HClO_4$
HBr	Br_2O, Br_3O_8, BrO_2	HBrO, $HBrO_3$
HI	I_2O_4, I_4O_9, I_2O_5	HIO, HIO_3, HIO_4, H_5IO_6

It is interesting to note that the most strongly electronegative element, fluorine, whose atoms are the smallest of the family and whose electrons are the most firmly held, does not show these higher oxidation states. It does form two oxides, F_2O and F_2O_2; but even here fluorine is in an oxidation state of − 1.

Before considering these compounds as individuals it is desirable to explain the system of naming the various acids and salts that has come into general use, not only for those of the halogens but for those of all the acid-forming elements.

Names of Acids and Their Salts · Compounds of any kind that consist of but two elements are called *binary* compounds. Examples of binary *acids* are HCl, HI, H_2S. These acids are given names beginning with the prefix *hydro-* and ending in *-ic*; examples are hydrochloric acid and hydrosulfuric acid (H_2S). Salts of these acids have names ending in *-ide*; examples are sodium chloride and ferrous sulfide (FeS).

Compounds of any kind that consist of three elements are called *ternary* compounds. Most ternary *acids* contain oxygen and hydrogen in addition to an acid-forming element, and are called oxygen acids. The best-known acid of a given acid-forming element is given a name ending in *-ic*. Examples are nitric acid and sulfuric acid. The salts of such acids have names ending in *-ate*, as sodium sulfate and potassium phosphate (K_3PO_4). An acid with less oxygen than the *-ic* acid has a name ending in *-ous*, as nitrous acid (HNO_2) and phosphorous acid (H_3PO_3); and the name of the derived salt ends in *-ite*, as sodium nitrite ($NaNO_2$) and potassium phosphite (K_2HPO_3). If there should be an acid of still less oxy-

gen content, its name begins with *hypo-* and ends in *-ous*, as hypophosphorous; while the salt will have the ending *-ite*, as sodium hypochlorite or potassium hypophosphite. Sometimes there is an acid with still more oxygen than the best-known one, and the name then begins with *per-*, as perchloric acid. The salts of perchloric acid are perchlorates.

The acids of the halogen elements illustrate all these usages, and both acids and their salts may be tabulated as follows, the chlorine derivatives being used as an example:

ACIDS AND SALTS CONTAINING CHLORINE			
ACID		SODIUM SALT	
Hydrochloric	HCl	Sodium chloride	$NaCl$
Hypochlorous	$HClO$	Sodium hypochlorite	$NaClO$
Chlorous	$HClO_2$	Sodium chlorite	$NaClO_2$
Chloric	$HClO_3$	Sodium chlorate	$NaClO_3$
Perchloric	$HClO_4$	Sodium perchlorate	$NaClO_4$

A salt having the formula $NaHSO_4$ is called sodium acid sulfate, sodium hydrogen sulfate, or, by an older name, sodium bisulfate.

The Oxides of Chlorine · The four known oxides of chlorine, namely, Cl_2O, Cl_2O_7, ClO_2, and Cl_2O_6, are all unstable, endothermic compounds. A brief discussion of three of these follows:

1. **Chlorine monoxide (hypochlorous anhydride) (Cl_2O).** This compound is prepared by passing chlorine through a tube containing mercuric oxide:

$$2\,Cl_2 + 2\,HgO \longrightarrow HgO \cdot HgCl_2 + Cl_2O\uparrow$$

It is a highly explosive, yellow gas, which condenses to a liquid at about 5°. With water it forms *hypochlorous acid.*

2. **Chlorine heptoxide (perchloric anhydride) (Cl_2O_7).** This oxide is a colorless, oily liquid and explodes with great violence when brought into contact with easily oxidizable material or when struck. With water it forms *perchloric acid.*

3. **Chlorine dioxide (ClO_2).** Chlorine dioxide is a yellow gas which may be condensed to a liquid boiling at about 10°. It reacts with water to form a mixture of chlorous and chloric acids:

$$2\,ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$$

Oxygen Acids of Chlorine · Chlorine forms a number of ternary compounds with oxygen and hydrogen. These are all acidic. In them the oxidation state of chlorine is $+1$, $+3$, $+5$, and $+7$. Fundamentally they are *hydroxides of chlorine,* as is shown by their structures.

Hypochlorous Acid and the Hypochlorites · The simplest hydroxide of chlorine is ClOH, whose electronic and structural formulas are

$$:\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{O}}:H \qquad Cl{-}O{-}H$$

In this compound chlorine has an oxidation state of + 1. Hypochlorous acid ionizes to give the ions H^+ and ClO^-, and the acid is usually written HClO. Both free hypochlorous acid and its salts (namely, the *hypochlorites*) are unstable. For this reason the acid has been obtained in dilute solution only.

1. **Preparation.** Hypochlorous acid forms as a product of an equilibrium reaction when chlorine is dissolved in water (p. 249):

$$Cl_2 + H_2O \rightleftarrows HCl + HClO$$

This reaction is unusual in that it leads to the formation of *two* acids, one of which (HCl) is very strong and the other (HClO) very weak. If powdered calcium carbonate is suspended in the water into which chlorine is passed, the strong acid reacts with it as fast as formed and is removed as a factor in the equilibrium. This brings about a much larger production of hypochlorous acid (which does not decompose calcium carbonate). By distilling the resulting mixture a dilute solution of hypochlorous acid is obtained. A similar dilute solution can also be obtained by treating a salt of the acid with dilute sulfuric acid and distilling the product.

Dilute solutions of the hypochlorites of sodium, potassium, and calcium are formed, along with their chlorides, when chlorine is passed into *cold* solutions of their respective hydroxides. With sodium hydroxide the reactions proceed thus:

$$Cl_2 + H_2O \longrightarrow \begin{cases} HClO & HClO + NaOH \longrightarrow NaClO + H_2O \\ + & \\ HCl & HCl + NaOH \longrightarrow NaCl + H_2O \end{cases}$$

These equations, when combined, give the following:

$$Cl_2 + 2\ NaOH \longrightarrow NaClO + NaCl + H_2O$$

2. **Properties.** Both hypochlorous acid and the hypochlorites, in water solution, are excellent oxidizing and bleaching agents. In the presence of a substance that will combine with the oxygen formed, they decompose as follows:

$$HClO \longrightarrow HCl + O \qquad KClO \longrightarrow KCl + O$$

On the other hand, when their solutions *are heated,* hypochlorous acid changes into the more stable acids chloric and hydrochloric; and the hypochlorites change into chlorates and chlorides:

$$3\ HClO \longrightarrow HClO_3 + 2\ HCl \qquad 3\ KClO \longrightarrow KClO_3 + 2\ KCl$$

It is evident, therefore, that if one wishes to prepare hypochlorites, *the solutions must be kept cold.*

The last two reactions are good examples of *autoxidation*, a type of reaction in which the same compound acts both as an oxidizing agent and as a reducing agent. Note that the chlorine in one of the three HClO molecules involved changes from an oxidation state of +1 to +5, while the chlorine in the other two is reduced from an oxidation state of +1 to −1. This is also true of the three KClO molecules.

Bleaching Powder ($CaOCl_2$) · When chlorine is passed into a cold solution of calcium hydroxide (ordinary slaked lime in water), there is formed a mixture of the chloride and hypochlorite of calcium, as explained above; if passed over calcium hydroxide in the form of a dry powder, however, a white solid compound is formed, known commercially as *bleaching powder* or *chloride of lime*:

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

The reaction is never complete, however, so that the commercial product always contains some unchanged calcium hydroxide.

The Constitution and Reactions of Bleaching Powder · The constitution of bleaching powder is not known with certainty, but is generally regarded as represented by the formula $Ca^{++}, \begin{matrix} Cl^- \\ ClO^- \end{matrix}$; in other words, it is a salt of both hydrochloric acid and hypochlorous acid. We may regard it as formed by replacing a hydrogen ion of each of these acids by an ion of bivalent calcium, thus:

$$Ca^{++}, \begin{matrix} OH^- \\ OH^- \end{matrix} + \begin{matrix} H^+, Cl^- \\ H^+, ClO^- \end{matrix} \longrightarrow Ca^{++}, \begin{matrix} Cl^- \\ ClO^- \end{matrix} + 2\,H_2O$$

Accordingly, if bleaching powder is treated with an acid of high boiling point, such as sulfuric acid (Chap. 22), we should expect both hydrochloric acid and hypochlorous acid to be evolved; and this is what actually happens. If the solutions used are concentrated, then the two acids evolved react with each other to form free chlorine, and the reactions may be represented as follows:

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4\downarrow + HCl + HClO$$
$$HCl + HClO \longrightarrow H_2O + Cl_2\uparrow$$

If in place of sulfuric acid there is added a very weak acid, like carbonic, which ionizes to a very limited extent, *only hypochlorous acid is formed*:

$$Ca^{++}, \begin{matrix} Cl^- \\ ClO^- \end{matrix} + H^+, HCO_3^- \longrightarrow Ca^{++}, \begin{matrix} Cl^- \\ HCO_3^- \end{matrix} + H^+, ClO^-$$

This is the reaction that takes place when bleaching powder is exposed to air, the carbonic acid being formed from the carbon dioxide and moisture in the air. The hypochlorous acid is evolved slowly and is a good disinfectant.

Manufacture and uses of bleaching powder. Bleaching powder is made in large quantities by passing chlorine into large rooms at *A* (Fig. 16-10), over the floors of which is spread a layer of calcium hydroxide. The excess of chlorine leaves the room at *B* and enters a similar room at *C*. The resulting product is used commercially as a source of chlorine, since it is easily prepared and transported and the chlorine present can be liberated as desired. The commercial product usually contains from 35 to 37 per cent of available chlorine. It readily loses chlorine, however, especially at summer temperatures. It is stored and shipped in airtight packages or iron drums, to prevent decomposition from contact with air.

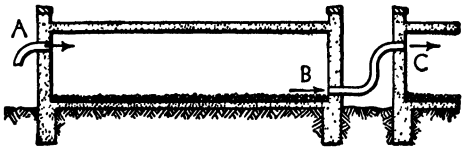
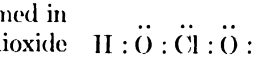


Fig. 16-10. Preparation of Bleaching Powder

Uses of the Hypochlorites · The hypochlorites, as well as the free acid, are excellent oxidizing and bleaching agents (p. 279). They also have a strong germicidal action. Many hypochlorite preparations are sold under various names by druggists, for use as disinfectants and antiseptics, and, if freshly prepared, are very efficient. Bleaching powder is used in large quantities for the same purposes, but liquid chlorine is displacing it to a large extent, as in the purification of water supplies and in bleaching.

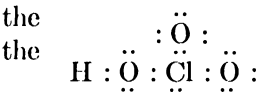
Chlorous Acid and the Chlorites · Chlorous acid is formed in small quantities, along with chloric acid, when chlorine dioxide is dissolved in water:



$$2\,ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$$

If this solution is neutralized with potassium hydroxide, a mixture of potassium chlorite and potassium chlorate results. Very recently methods have been developed for the industrial production of chlorites. They are coming into use as oxidizing agents in place of hypochlorites.

Chloric Acid and the Chlorates · Chlorates are formed when chlorine is passed into *hot* solutions of the hydroxides of the metals (p. 278). A typical reaction is expressed by the following equations:



$$3\,Cl_2 + \cancel{3\,H_2O} \rightleftarrows \cancel{3\,HCl} + \cancel{3\,HClO} \qquad (1)$$

$$6\,KOH + \cancel{3\,HCl} + \cancel{3\,HClO} \rightleftarrows 3\,KCl + \cancel{3\,KClO} + \cancel{6}^{3}H_2O \qquad (2)$$

$$\cancel{3\,KClO} \xrightarrow{\Delta} 2\,KCl + KClO_3 \qquad (3)$$

$$3\,Cl_2 + 6\,KOH \longrightarrow 5\,KCl + KClO_3 + 3\,H_2O \qquad (4)$$

Thus equation (4) results from the addition of equations (1), (2), and (3).

When the resulting solution is evaporated, the potassium chlorate, being much less soluble than the potassium chloride, separates first, and by repeated crystallization can be obtained in the pure state.

The series of equations above forms a good example of a chemical reaction that takes place in steps. The first reaction is the action of chlorine on water (p. 278). The equation is multiplied by 3 so that all the equations will deal with equivalent amounts. The second reaction is the neutralization of the acids from equation (1). The third equation shows the autoxidation of KClO, which takes place when the latter is heated. By canceling out all products which are formed in one step and used in a subsequent step, or which are used in one step and formed in another, we may add the equations to give a balanced equation for the over-all reaction, showing the reactants and final products only. The chemist, by using his knowledge of the steps in the reaction, can often arrive at the nature and amounts of the final products, as was done in this case.

From the chlorates, chloric acid itself can be prepared. The most convenient method consists in adding the calculated quantity of sulfuric acid to an aqueous solution of barium chlorate:

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2\ HClO_3$$

The insoluble barium sulfate separates as a white precipitate, which is removed by filtration, leaving a solution of chloric acid. This may be concentrated until it contains 40 per cent of acid. Further concentration leads to the decomposition of the acid, forming perchloric acid, water, and chlorine dioxide. The concentrated aqueous solution of the acid is a colorless liquid and has powerful oxidizing properties.

The chlorates can readily be obtained in the pure state, and are all soluble in water. Potassium chlorate and sodium chlorate are the most important of these salts.

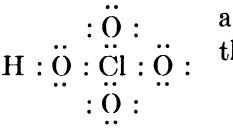
Commercial methods for preparing hypochlorites and chlorates. The method of preparing chlorates by passing chlorine into hot solutions of the hydroxide is a simple one but not economical. For example, in the case of potassium chlorate it will be seen, by reference to equation (4), that only one sixth of the potassium in the hydroxide used is converted into the chlorate. Electrolytic methods are now used almost entirely for the preparation of both hypochlorites and chlorates.

It will be recalled that the electrolysis of a solution of potassium chloride or of sodium chloride results in the formation of chlorine, together with the corresponding hydroxide of the metal. It is possible so to regulate this process that the chlorine, instead of being evolved, is retained in the solution, together with the hydroxide, with which it interacts to form either the hypochlorite or chlorate.

Perchloric Acid and the Perchlorates · When potassium chlorate is heated, a portion of the compound changes into the perchlorate:

$$4\,KClO_3 \longrightarrow 3\,KClO_4 + KCl$$

This reaction serves as a convenient method for preparing perchlorates, and perchloric acid itself can be obtained from these by the addition of sulfuric acid:



$$KClO_4 + H_2SO_4 \longrightarrow KHSO_4 + HClO_4$$

The perchloric acid formed is separated by distillation under diminished pressure (Fig. 16-11), and, in the case of so strong an oxidizing agent, is distilled in an apparatus provided with ground-glass joints rather than with cork or rubber connections.

Pure perchloric acid is a colorless liquid. It is unstable, sometimes decomposing spontaneously with great violence. Like the other oxygen acids of chlorine, it is an oxidizing agent. A concentrated solution of

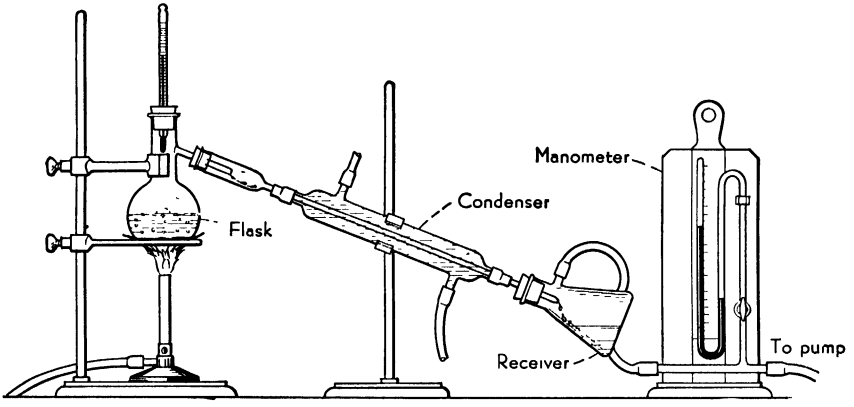


Fig. 16-11. Distillation under Diminished Pressure

perchloric acid is now an article of commerce and finds a number of applications in analytical chemistry.

The perchlorates are readily prepared pure and are the most stable of all the salts of the oxygen acids of chlorine. When heated to high temperatures, they decompose into oxygen and the corresponding metal chlorides. Potassium perchlorate is one of the few compounds of potassium that are nearly insoluble in water (and still less soluble in alcohol), and advantage is taken of this property in an analytical procedure for determining the percentages of potassium present in different substances. Both chlorates and perchlorates are used as oxidizing agents, although the latter are gaining in favor because they are less hazardous.

Reactions taking place in the preparation of oxygen. It will be recalled that oxygen is commonly prepared in the laboratory by heating potassium chlorate. It is evident from the statements given above that two reactions take place concurrently when the potassium chlorate is heated: (1) the larger part is directly decomposed into potassium chloride and oxygen, and (2) the remainder is converted into potassium perchlorate and potassium chloride. The perchlorate, on further heating, is decomposed into the chloride and oxygen, so that all the oxygen in the potassium chlorate is ultimately evolved.

The oxygen acids of bromine and their salts. Three oxides of bromine are known, namely, Br_2O, Br_3O_8, and BrO_2; and the following oxygen acids have been prepared in dilute solutions: hypobromous acid (HBrO) and bromic acid ($HBrO_3$). The hypobromites and bromates are very similar to the corresponding chlorine compounds and are prepared by the same general methods. From these salts the free acids can be prepared, as in the case of the corresponding chlorine compounds. The hypobromites are sometimes used as oxidizing agents, decomposing into oxygen and the corresponding bromide.

Iodine Pentoxide (I_2O_5) · Several oxides of iodine are known, of which the pentoxide is the most interesting. This is a white solid formed by heating iodic acid to 200°:

$$2\ HIO_3 \rightleftarrows H_2O + I_2O_5$$

The reaction is reversible, for the oxide combines with water at ordinary temperatures to form iodic acid. At high temperatures it is decomposed into its constituent elements and acts as an oxidizing agent.

Iodic Acid (HIO_3) · This acid is formed by the action of sulfuric acid upon the iodates, although it is more convenient to prepare it by oxidizing iodine directly with nitric acid. It forms white crystals and is a strong oxidizing agent. A number of salts of iodic acid are known but are of relatively little importance. The principal source of iodine is sodium iodate, $NaIO_3$, and especially *lautarite*, calcium iodate, $Ca(IO_3)_2$, both found in the *caliche*, or nitrate ore of Chile saltpeter (p. 296).

Anhydrides of Acids and of Bases · In the last equation it will be noticed that the oxide I_2O_5 can combine with water to form iodic acid. Many nonmetallic oxides can combine with water in a similar way to form acids (p. 53), and such oxides are called *anhydrides* of the acids, or *acid anhydrides.*

Many metallic oxides (p. 53) can combine with water to form bases, and such oxides are called anhydrides of bases, or *basic anhydrides.*

QUESTIONS

1. (*a*) List a number of similarities and differences in the properties of the halogens. (*b*) To what can these be attributed?

2. Which halogen (*a*) forms a hydride which etches glass? (*b*) is a liquid at room temperature? (*c*) accumulates in the thyroid gland? (*d*) is a solid at room temperature? (*e*) does not occur in nature? (*f*) forms the most unstable hydride? (*g*) has the greatest electron affinity of all the elements? (*h*) reacts most vigorously with water? (*i*) has oxidation states of -1, $+1$, $+3$, $+5$, and $+7$? (*j*) cannot be prepared from a water solution?

3. How do you account for the change in the stability of the hydrogen halides with increasing molecular weight?

4. Starting with sodium chloride, show by equations how you would prepare sodium hypochlorite (NaClO).

5. Why do none of the halogens occur free in nature?

6. Complete and balance the following equations by the oxidation-state method:

a. $HCl + MnO_2 \longrightarrow$
b. $NaBr + H_2SO_4 + KMnO_4 \longrightarrow$
c. $NaBr + H_2SO_4 + MnO_2 \longrightarrow$
d. $I^- + H^+ + SO_4^{--} + MnO_2 \longrightarrow$
e. $Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^-$

7. Iodine melts at 113.5° and boils at 184.4°. Why can it be purified by sublimation rather than by distillation?

8. What names would you give to the following acids and their salts: (*a*) H_2SO_4; (*b*) H_2SO_3; (*c*) H_2SO_2; (*d*) H_3PO_4; (*e*) H_3PO_3; (*f*) H_3PO_2?

9. What method of preparation is applicable alike to chlorine, bromine, and iodine?

10. How can you effect the following changes: (*a*) $I_2 \longrightarrow HI$; (*b*) $NaBr \longrightarrow NaCl$; (*c*) $NaCl \longrightarrow NaBr$; (*d*) $K_2SO_4 \longrightarrow KI$; (*e*) $NaBr \longrightarrow NaI$?

11. Suppose you were given three bottles, each containing one of the following compounds: potassium iodide, sodium chloride, and potassium bromide, and were required to distinguish between them. How would you proceed?

12. Why should sulfuric acid and carbonic acid act differently on bleaching powder?

13. (*a*) Enumerate the uses of the halogens and some of their compounds. (*b*) What properties make them suitable for these uses?

PROBLEMS

1. If you had to prepare 100 g of silver iodide, (*a*) how would you proceed? (*b*) what weight of each of the compounds used would be required?

2. One liter of tincture of iodine contains 70 g of iodine and 50 g of potassium iodide dissolved in dilute alcohol. Suppose you were supplied with potassium iodide but not with free iodine. (*a*) How would you proceed to prepare the tincture? (*b*) What weight of potassium iodide would be required?

3. Calculate the percentage composition of potassium iodate (KIO_3).

4. On analysis, a compound was found to have the composition 28.22 per cent potassium; 46.19 per cent oxygen; 25.58 per cent chlorine. (*a*) What formula do you calculate for the compound? (*b*) Is this the only possible formula?

5. Indicate the electrovalence, the covalence, and the oxidation state of the elements in the following compounds: (*a*) potassium hypochlorite; (*b*) potassium chlorite; (*c*) potassium chlorate; (*d*) potassium perchlorate.

CHAPTER 17

THE ALKALI METALS

A survey of the known elements indicates that they can be classified as (1) metals — those that have a metallic luster and whose oxides form bases — and (2) nonmetals — those that do not have a metallic luster and whose oxides form acids. We have already found (Chap. 16) that the halogen family is a typical group of nonmetals and that their atoms all have seven valence electrons, which give them similar properties. We are now ready to study a typical group of metals, known as the alkali metals; these are lithium, sodium, potassium, rubidium, cesium, and francium, all of which have one valence electron per atom.

Properties · The alkali metals are called a *family* of elements because their properties and atomic structure are similar. Their electron configurations and atomic and ionic diameters are given in the following table:

THE ALKALI METALS AND THEIR PROPERTIES

ELEMENT	ATOMIC WEIGHT	AT. NO.	DENSITY	MELTING POINT	IONIC DIAM*	ATOMIC DIAM*	DISCOVERER	ELECTRONS IN SHELLS
Lithium (Li)	6.940	3	0.53	186.0°	1.20	3.04	Arvedson, 1817	2, 1
Sodium (Na)	22.997	11	0.97	97.5°	1.90	3.72	Davy, 1807	2, 8, 1
Potassium (K)	39.096	19	0.86	62.3°	2.66	4.62	Davy, 1807	2, 8, 8, 1
Rubidium (Rb)	85.48	37	1.53	38.5°	2.96	4.88	Bunsen, 1861	2, 8, 18, 8, 1
Cesium (Cs)	132.91	55	1.90	26.0°	3.38	5.24	Bunsen, 1860	2, 8, 18, 18, 8, 1
Francium (Fr)	—	87	—	—	—	—	Percy, 1939	2, 8, 18, 32, 18, 8, 1

*Diameter in angstrom units. (Å)

The reason for their similar properties is now obvious; the electron configurations of the outer shells are similar. In so far as there are differences in properties, we would assume that the properties change progressively from lithium to cesium because the number of inner shells increases progressively. The properties of francium are not yet clearly enough defined to be included in this discussion.

The alkali metals all form ions with an electrovalence of $+1$; their hydroxides are strong bases; their compounds have similar formulas; and most of their compounds are soluble.

As free elements, the alkali metals are very soft, probably because their atoms are relatively large (see the table above). Their reactivity and relative ease of oxidation are indicated by their position near the top of the electrochemical series (p. 88), and are to be explained

by the ready removal of the one valence electron. Cesium is the most reactive of all the metals, including the other alkali metals. The elements of this family also form the most strongly basic hydroxides (alkalies) known; hence the name *alkali* metals.

Occurrence · Since the alkali metals are very reactive, we can expect to find them in the combined, rather than the free, state in nature. Furthermore, the high solubility of most of their compounds would indicate that they would be found in the ocean, in dead seas, or in salt beds well protected from the erosion action of ground water. In general, all this is true.

In the earth's crust they may all have occurred originally as complex silicates; all primitive rocks contain minerals of this kind. The erosion processes of nature have decomposed great quantities of these silicates, liberating their active metals in the form of simple ions.

PER CENT OF ALKALI METALS IN NATURE

METAL	PER CENT IN IGNEOUS ROCKS	PER CENT IN SEA WATER
Sodium	2.85	2.8
Potassium	2.60	0.08
Lithium	4×10^{-5}	—
Rubidium	1×10^{-6}	—
Cesium	1×10^{-7}	—
Francium	—	—

Francium occurs only in small amounts in nature; it is produced by nuclear reactions (Chap. 21). Lithium, sodium, potassium, and rubidium have been detected in the sun by the spectroscope. Most plants contain much more potassium than sodium. The principal sources of several of these elements are given in the following table:

CHIEF SOURCES OF SEVERAL ALKALI METALS

METAL	MINERAL	FORMULA
Lithium	Amblygonite Spodumene Lepidolite	$Li\,(Al, F)PO_4$ $LiAl(SiO_3)_2$ $KLi_2Al(Si_4O_{10})(OH, F)_2$
Sodium	Halite (rock salt)	$NaCl$
Potassium	Carnallite Sylvite	$KCl \cdot MgCl_2 \cdot 6\,H_2O$ KCl
Rubidium	Occurs in traces in several minerals	
Cesium	Pollucite	$H_2Cs_4Al_4(SiO_3)_9$

Flame Tests · When even a very small amount of a compound of one of these elements is heated directly in a Bunsen-burner flame, the flame

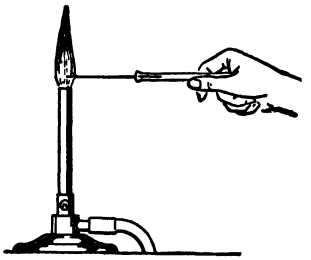


Fig. 17-1. Method of Making a Flame Test · The end of a clean platinum wire is dipped into water and rubbed in the substance to be tested (or dipped into a concentrated solution of the substance). The wire, with the adhering particles, is then held in the outer edge of the base of the Bunsen flame

acquires a color characteristic of the element: red for lithium, yellow for sodium, violet for potassium, blue-red for rubidium, and blue for cesium. The production of colored flames makes a sensitive test for the presence of these elements; a definite color is imparted to the flame with only 10^{-10} g of sodium and with about five thousand times this quantity of potassium. Observation of these flames with a spectroscope shows colored lines at definite wave lengths (p. 122) and increases the sensitivity of the method as an analytical tool.

Preparation of the Metals · The alkali metals can be prepared by the electrolysis of the fused hydroxide or chloride in a special cell which protects the molten metal from oxidation by the oxygen in the air (see Fig. 17-2). The commercial process in the United States uses the chloride.

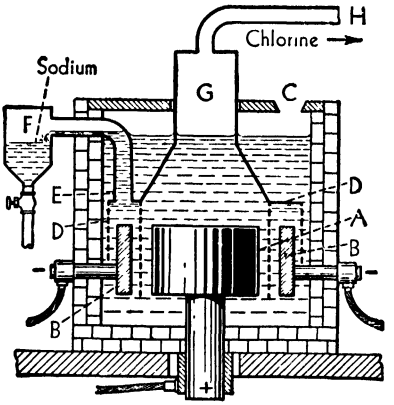


Fig. 17-2. Diagram of the Downs Cell for the Production of Sodium · The essential parts of the Downs cell are as follows: *A* represents the anode (made of graphite), and *B*, *B*, an annular iron or steel cathode, which is surrounded by the annular compartment *D*, *D*. The melted sodium chloride is admitted at *C*. When the current is turned on, the sodium liberated at the cathode *B*, *B*, being very light, rises to the top of the compartment, flows upward through the tube, *E*, and over into the container, *F*, from which it is withdrawn from time to time. The chlorine escaping from the anode, *A*, rises in the dome, *G*, and escapes through the pipe, *H*

These metals may be prepared also by reducing their hydroxides or carbonates at moderately high temperatures with such reducing agents as carbon, iron, and calcium. Because of the easy volatility of cesium, this metal is best obtained by heating the chloride with metallic calcium and distilling off the cesium:

$$2\ CsCl + Ca \longrightarrow CaCl_2 + 2\ Cs$$

Uses of the Metals · Sodium is the only one of these metals that has a wide commercial use. It is now produced by the ton and sold in large bricks or even in tank-car lots for the manufacture of soap, organic chemicals, dyes, tetraethyl lead, sodium cyanide, sodium peroxide, and a variety of other products. It has been used to fill the centers of exhaust valves of aircraft engines, for sodium-vapor lamps, and to alloy with lead for electric-cable sheathing. Cesium and rubidium are used to a limited extent in photoelectric cells because these metals emit electrons under the influence of light of ordinary wave lengths.

Reactions of the Metals · This family of metals represents one of the most reactive groups of metals known. They react with oxygen to form oxides and peroxides, with hydrogen to form hydrides, with water to release hydrogen, and with many of the other nonmetals. The hydrides of these metals are of interest because they are analogous to the alkali halides; on electrolysis of the molten hydride, hydrogen is liberated at the anode (p. 215), which indicates that the hydrogen has a negative charge. In liquid ammonia any one of these metals dissolves to form highly conducting solutions from which the metal can be removed unchanged by evaporation of the solution. The conductivity of these solutions is explained by the assumption that the metal atoms ionize to give positive metal ions and solvated electrons. In the presence of a catalyst or on long standing, they react with the ammonia to evolve hydrogen. They dissolve in mercury to form amalgams and in a number of other metals to form alloys.

Compounds of the Metals · These elements are better known by the compounds that they form than as free metals. Some of their compounds are among the most commonly used chemicals (see the table below).

SOME COMPOUNDS OF THE ALKALI METALS

COMPOUND		COMMON NAME AND USE
Name	Formula	
Sodium chloride . .	NaCl	Table salt; manufacture of chlorine, lye, and other sodium compounds
Sodium hydroxide .	NaOH	Lye
Sodium sulfate . .	Na_2SO_4	Manufacture of paper and glass
Sodium bicarbonate	$NaHCO_3$	Baking soda
Sodium carbonate .	Na_2CO_3	Soda ash; manufacture of glass
Sodium nitrate . .	$NaNO_3$	Fertilizer; manufacture of nitric acid
Potassium nitrate .	KNO_3	Saltpeter; fertilizer; manufacture of black powder
Potassium carbonate	K_2CO_3	Potash; manufacture of soap and hard glass; textile industry

Except for lithium carbonate and lithium phosphate, which are sparingly soluble, the common compounds of this family are soluble.

Typical yearly production figures for some of the sodium compounds in the United States are given in the following table:

APPROXIMATE YEARLY PRODUCTION OF SODIUM COMPOUNDS

COMPOUND	TONS	COMPOUND	TONS
Chloride	16,650,000	Bicarbonate	200,000
Carbonate	4,375,000	Phosphate	470,000
Hydroxide	2,280,000	Chromate	90,000
Silicate	500,000	Metal	80,000 (est.)
Sulfate	1,000,000		

In general, the methods of preparation of the compounds of these metals are similar because of their similar properties. The compounds of sodium have considerably wider use because they are more abundant and far less expensive than those of the other metals.

Lithium and Its Compounds

Lithium · Lithium is the lightest of all metals that are solid at ordinary temperatures; it has a density of 0.53. It forms many compounds, but only a few are of any commercial importance. It forms a nitride readily by direct combination with nitrogen at ordinary temperatures. In metallurgy, minute quantities of lithium degasify copper alloys and lead to a fine grain size for metallic magnesium.

Uses of Lithium Compounds · *Lithium chloride* (LiCl) is prepared directly from the lithium minerals and, like the carbonate, is used in the preparation of other lithium compounds; it has become important in connection with air-conditioning, since there is now an assured production of it. It is very soluble in water and has the property, unusual among inorganic salts, of being easily soluble in alcohol and in certain other nonaqueous solvents. Concentrated water solutions of this very soluble salt have a low vapor pressure, and air bubbled through such a solution has about the right humidity for comfort, about 50 per cent at 70°.

Lithium bromide (LiBr) and *lithium carbonate* (Li_2CO_3) are used in medicine; and in the ceramic industry *lithium oxide* (Li_2O) contributes more to the lowering of the melting point and viscosity of special glazes, glasses, and enamels than any other constituent which can be added.

The Compounds of Sodium

Preparation of Sodium Compounds · Sodium forms a large number of useful compounds, most of which are prepared from the chloride, since it is abundant and inexpensive. The processes involved are often not simple, because the sodium compounds to be prepared are usually soluble and therefore cannot be prepared directly from the chloride by precipitation. Experiments have shown that the most economical method of procedure consists either in first changing the chloride into the hydroxide by the electrolysis of its aqueous solution or in converting it into the carbonate by the methods to be described. Since the hydroxide is a base and the carbonate is a salt of a very weak volatile acid, both are readily changed into other compounds.

The common sodium salts are all inexpensive, and, being soluble, they serve as a convenient and cheap source of the various anions used in preparing the insoluble compounds of the metals by double decomposition.

Oxides of Sodium · If sodium is burned in a limited supply of oxygen at a controlled temperature, the expected (valence) oxide (Na_2O) can be prepared. It is a white powder and is a very powerful drying agent. In combining with water it can be made to form anhydrous sodium hydroxide. It attacks many substances, both inorganic and organic.

If the metal in the form of shavings is burned in an abundant current of air, the peroxide, Na_2O_2, is formed. Treated with water or dilute acids, it yields hydrogen peroxide:

$$Na_2O_2 + 2\ H_2O \longrightarrow 2\ NaOH + H_2O_2$$
$$Na_2O_2 + 2\ HCl \longrightarrow 2\ NaCl + H_2O_2$$

Sodium peroxide is an important source of hydrogen peroxide, as well as of many other peroxides, peracids, and salts, such as perborates and percarbonates. All these compounds are strong oxidizing agents.

Sodium Hydroxide (Caustic Soda) (NaOH) · This compound is prepared on a large scale by two general processes.

1. **Action of calcium hydroxide upon sodium carbonate.** This process consists in treating calcium hydroxide suspended in water with a solution of sodium carbonate. The reaction takes place in accordance with the following equation:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2\ NaOH$$

The calcium hydroxide is only slightly soluble in water (about 1.6 g in 1000 ml at ordinary temperatures), but more so than the calcium carbonate. As fast as the dissolved hydroxide acts with the sodium carbonate, more of it

passes into solution to continue the reaction. The calcium carbonate separates as fast as formed, and when the reaction is complete it is removed by filtration. The sodium hydroxide dissolved in the filtrate is obtained by evaporation.

2. **Electrolytic methods.** We have seen that an electric current, passed through a solution of sodium chloride, produces both chlorine and sodium hydroxide (p. 232), and that this process constitutes an important source of sodium hydroxide, as well as of chlorine. It is not practicable to decompose *all* the sodium chloride by electrolysis, so that the resulting solution contains both sodium chloride and sodium hydroxide. The chloride is much less soluble than the hydroxide; and when the solution is partially evaporated, the chloride separates, leaving a nearly pure solution of hydroxide. This is evaporated to dryness, and the sodium hydroxide is melted to drive off all the water. As it cools, the product solidifies as a white solid and is sold in this form.

The product prepared by either of the methods above is never pure. If desired, it may be further purified by treatment with alcohol, which dissolves the sodium hydroxide but only small amounts of the impurities. Perfectly pure sodium hydroxide may best be obtained by the action of sodium on water and the evaporation of the resulting solution.

Properties of Sodium Hydroxide · This compound is a white, crystalline, brittle solid. For laboratory purposes it is ordinarily sold in the form of sticks, in shape resembling sticks of candy, or as pellets, or as white flakes. It is often called *caustic soda*. As this name indicates, it is a corrosive substance and has a strong disintegrating action upon both animal and vegetable tissues. When exposed to the air, it absorbs both moisture and carbon dioxide and is changed into sodium carbonate. It is extremely soluble in water, and a great deal of heat is liberated in the process of solution. Its solution has a soapy feel and a strong cleansing action.

Production and Uses of Sodium Hydroxide · About 2,280,000 tons of sodium hydroxide is produced annually in the United States, more than half of which is prepared by the electrolytic process. The compound is used in many chemical industries. Some idea of its importance can be gained from the fact that it is used in the manufacture of all hard soaps. If, as is sometimes stated, the state of civilization of a country can be told by the amount of soap it consumes, then the same statement will hold for the amount of caustic soda used. Large quantities are also used in the manufacture of rayon and various chemicals, in the refining of petroleum, and in preparing wood pulp from which paper is made; see the table on the following page.

CONSUMPTION OF SODIUM HYDROXIDE IN THE UNITED STATES

USE	TONS	USE	TONS
Rayon and film	500,000	Petroleum	160,000
Chemicals	650,000	Lye	130,000
Exports	185,000	Textiles	100,000
Soap	145,000	Pulp and paper	170,000

Sodium Chloride (NaCl) · This compound was discussed in Chapter 14.

Sodium Sulfate (Na_2SO_4) · Large deposits of this salt occur in the United States and Canada. It is also obtained as a by-product in the manufacture of hydrochloric acid (p. 251). It has many uses, including its use in the manufacture of rayon, of glass, and of paper.

Under usual conditions sodium sulfate crystallizes from water in the form of a decahydrate ($Na_2SO_4 \cdot 10\ H_2O$). This is known as *Glauber's salt*, from the alchemist Glauber, who lived about the middle of the seventeenth century and who first used the compound in medicine. The transition point between the decahydrate and the anhydrous salt is 32.38° (p. 198); this point can be used in the calibration of thermometers.

By the action of sulfuric acid, sodium sulfate is converted into the acid sulfate, $NaHSO_4$, commonly known as sodium bisulfate.

Sulfites of Sodium · The acid sulfite, $NaHSO_3$, often called sodium bisulfite, is formed by saturating a solution of sodium carbonate with sulfur dioxide. Sulfurous acid is first formed by the union of the dioxide with water, and this reacts with the carbonate as shown in the following equation:

$$Na_2CO_3 + 2\ H_2SO_3 \longrightarrow 2\ NaHSO_3 + H_2O + CO_2\uparrow$$

The normal sulfite, Na_2SO_3, is prepared by adding sodium carbonate to a saturated solution of the acid sulfite in the proportion indicated in the following equation:

$$2\ NaHSO_3 + Na_2CO_3 \longrightarrow 2\ Na_2SO_3 + H_2O + CO_2\uparrow$$

Both the sulfites readily absorb oxygen, forming the corresponding sulfates; they are therefore reducing agents. They are used to some extent as bleaching agents and as preservatives.

Sodium Thiosulfate ($Na_2S_2O_3$) · This salt is made by adding sulfur to a solution of sodium sulfite and warming the mixture:

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

Upon evaporation, the resulting solution yields the pentahydrate, $Na_2S_2O_3 \cdot 5\ H_2O$, which is commonly known as *hyposulfite of soda* or simply *hypo*.

Acids react with sodium thiosulfate, forming thiosulfuric acid, which decomposes as fast as formed into sulfur dioxide, water, and sulfur in colloidal form:

$$Na_2S_2O_3 + 2\,HCl \longrightarrow H_2S_2O_3 + 2\,NaCl$$
$$H_2S_2O_3 \longrightarrow H_2O + SO_2\uparrow + S\downarrow$$

The salt is used very largely in photography as a solvent for silver salts (see photography), and as an "antichlor" for removing any chlorine remaining in substances bleached with this element.

Sodium Carbonate (Soda Ash) (Na_2CO_3) · This very important compound has long been almost entirely a manufactured salt. Many years ago it was obtained by burning seaweeds, some of which are rich in compounds of sodium. When the weeds are burned, the resulting ashes contain the sodium as carbonate, which accounts for the name *soda ash*. In a similar way land plants and trees build up potassium compounds in their structures, and their ashes yield potassium carbonate. In more recent years sodium carbonate has been found to be a constituent of the salts of dried-up desert lakes, particularly of Searles Lake and Owens Lake in California. These deposits are worked for a number of salts, such as borax, potassium salts, sodium sulfate, and compounds of lithium. Along with these sodium carbonate is recovered to the extent of about 100,000 tons annually. Deep borings (300 ft) at Searles Lake disclosed unexpected and enormous deposits of both sodium carbonate and the bicarbonate.

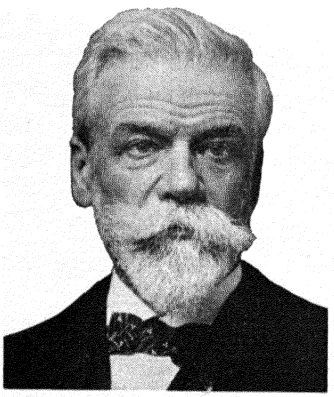


Fig. 17-3. Ernest Solvay (1835–1922) A famous Belgian chemical engineer who developed the Solvay process for the manufacture of sodium carbonate

The Manufacture of Sodium Carbonate; the Solvay Process · As a manufactured salt, the sodium carbonate used in the United States is made from sodium chloride, nearly all by a process devised by the Belgian chemical engineer Ernest Solvay (Fig. 17-3) and known as the *Solvay process*. In this process ammonia and carbon dioxide are passed into a concentrated solution of sodium chloride, and sparingly soluble sodium bicarbonate is formed. This bicarbonate precipitates, is removed by filtration, and is changed into the normal carbonate by heating.

Reactions Involved in the Solvay Process · Ammonia and carbon dioxide react with water to form ammonium hydroxide and carbonic acid respectively:

$$NH_3 + H_2O \longrightarrow NH_4OH \quad (1)$$

$$CO_2 + H_2O \longrightarrow H_2CO_3 \quad (2)$$

These then react with each other to form ammonium bicarbonate:

$$NH_4OH + H_2CO_3 \longrightarrow NH_4HCO_3 + H_2O \quad (3)$$

The ammonium bicarbonate and salt react to form sodium bicarbonate, which is only slightly soluble (in the presence of sodium ions) and precipitates:

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 \downarrow + NH_4Cl \quad (4)$$

The bicarbonate is removed by filtration and changed into the normal carbonate by heating:

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \uparrow \quad (5)$$

The "mother liquors" remaining after the precipitation of the sodium bicarbonate contain the ammonium chloride formed according to equation (4). These are treated with lime (CaO); this liberates the ammonia, which can thus be used again:

$$2\ NH_4Cl + CaO \longrightarrow CaCl_2 + H_2O + 2\ NH_3 \uparrow \quad (6)$$

The lime is obtained by heating limestone ($CaCO_3$):

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow \quad (7)$$

The ammonia liberated according to equation (6) and the carbon dioxide liberated according to equation (7) are utilized in the reactions represented by equations (1) and (2). Theoretically at least, the ammonia used in the process is all recovered (equation (6)) and so can be used over and over again.

Addition of the equations above shows that the over-all reaction has been to convert calcium carbonate and sodium chloride into calcium chloride and sodium carbonate:

$$CaCO_3 + 2\ NaCl \longrightarrow CaCl_2 + Na_2CO_3$$

Solubility considerations indicate that this reaction will not take place in solution in this direction (Chap. 25), since calcium carbonate is the least soluble of the four substances present. The Solvay process, therefore, consists in a mechanism for carrying out a reaction which does not take place directly. It is evident that calcium chloride is a by-product.

The Leblanc Process · The method devised by a French chemist, Leblanc, consists in heating sodium chloride with sulfuric acid, which results in the formation of sodium sulfate and hydrochloric acid (p. 251). The resulting sodium sulfate is then heated with a mixture of powdered coal and limestone. The carbon of the coal reduces the sodium sulfate to sodium sulfide (Na_2S), which then reacts with the calcium carbonate present in the limestone, forming sodium carbonate, thus:

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS$$

The Leblanc process has never been used to any extent in the United States.

Properties and Uses of Sodium Carbonate · The aqueous solution of sodium carbonate is basic in character (p. 457). With water the salt forms a number of different hydrates, the most common of which is the decahydrate, $Na_2CO_3 \cdot 10\ H_2O$. By cooling a hot solution of the salt, this hydrate is obtained in the form of large, clear, monoclinic crystals often known as *washing soda* or *sal soda.*

The decahydrate effloresces on exposure to dry air, changing into the monohydrate. The transition point of the decahydrate into the heptahydrate, $Na_2CO_3 \cdot 7\ H_2O$, is 32°, and of this into the monohydrate, 35.37°. The anhydrous salt melts at 851° and along with potassium carbonate is used for decomposing silicates. Mere mention of the fact that sodium carbonate is used in the manufacture of glass, soap, and many chemical reagents will indicate its importance in the industries. More than 4,400,000 tons is produced annually in the United States for these various uses, most of which is made by the Solvay process.

YEARLY CONSUMPTION OF SODIUM CARBONATE IN THE UNITED STATES

USE	TONS	USE	TONS
Glass	1,290,000	Pulp and paper	200,000
Soap	160,000	Water-softener	110,000
Chemicals	1,800,000 (est.)	Textiles	65,000
Cleaning compounds . .	110,000	Caustic and bicarbonate	700,000

Sodium Hydrogen Carbonate (Bicarbonate of Soda, or Baking Soda) ($NaHCO_3$) · This salt is prepared either by the Solvay process, as already explained, or by passing carbon dioxide into saturated solutions of sodium carbonate:

$$Na_2CO_3 + H_2O + CO_2 \rightleftarrows 2\ NaHCO_3\downarrow$$

The bicarbonate, being but sparingly soluble, precipitates. When the solid is heated, the reaction is reversed, and the bicarbonate changes into the carbonate, with liberation of carbon dioxide. The salt is used as an aerating agent in baking. For this purpose it must be mixed with some substance, such as sour milk, cream of tartar, or an acid phosphate (see baking powders), that slowly reacts with the carbonate, liberating carbon dioxide.

Sodium Nitrate (Chile Saltpeter) ($NaNO_3$) · This substance is found in certain arid regions where it has apparently been formed by the decay of organic substances in the presence of air and sodium salts. The largest deposits are in Chile, and most of the natural nitrate of commerce comes from that country. Smaller deposits occur in California and Texas. The

crude nitrate is known as *caliche*. Large quantities of sodium nitrate are used in the manufacture of fertilizers.

Sodium Cyanide (NaCN) · This salt of hydrocyanic acid (HCN) is prepared from sodium. The sodium is first changed into sodamide (p. 398). The latter is then converted into sodium cyanide by heating with carbon:

$$NaNH_2 + C \longrightarrow NaCN + H_2\uparrow$$

An increasing amount of the salt is also being made by heating a mixture of calcium cyanamide and carbon (Chap. 36) with sodium chloride. When sodium cyanide is exposed to air, hydrocyanic acid is liberated through the action of the moisture and carbon dioxide in the air. The aqueous solution of the salt is alkaline. A solution of the salt readily dissolves gold and is used for extracting this metal when it is scattered in small quantities through earthy material. It is also used in electroplating baths, as well as in the manufacture of hydrocyanic acid. Like the acid, it is extremely poisonous.

Sodium Phosphates · Since phosphorus forms a number of acids, most of which are polybasic, one can readily understand why so many different phosphates of sodium are known. Some of these are discussed in Chapter 23.

The common phosphate used in the laboratory is the *disodium phosphate*, Na_2HPO_4. This salt is present in our blood and urine, and it was from these sources that the compound was first obtained. It is prepared industrially by the action of phosphoric acid on sodium carbonate:

$$Na_2CO_3 + H_3PO_4 \longrightarrow Na_2HPO_4 + H_2O + CO_2\uparrow$$

The salt crystallizes from the solution in the form of the hydrate, $Na_2HPO_4 \cdot 12\ H_2O$.

The normal *sodium phosphate* is obtained by the action of sodium hydroxide on the disodium salt:

$$Na_2HPO_4 + NaOH \rightleftarrows Na_3PO_4 + H_2O$$

When the solution is evaporated, crystals that have the formula $Na_3PO_4 \cdot 12\ H_2O$ separate. The aqueous solution of the salt is strongly basic in reaction. When sodium phosphate is added to hard waters, the calcium and magnesium salts are precipitated as phosphates, and the water is left basic in reaction; hence the use of the salt to soften hard waters in our homes and in laundries.

Monosodium phosphate is formed by the action of phosphoric acid on the disodium salt:

$$H_3PO_4 + Na_2HPO_4 \longrightarrow 2\ NaH_2PO_4$$

Other Compounds of Sodium · *Sodium bromide* (NaBr) and *sodium iodide* (NaI) resemble sodium chloride in their properties. They can be prepared by the action of bromine and iodine, respectively, upon a solution of sodium hydroxide, the reaction being similar to that of chlorine upon bases (p. 278). They are used in medicine and in preparing silver bromide and silver iodide for photographic purposes. Both the acid and the normal salts of hydrosulfuric acid,

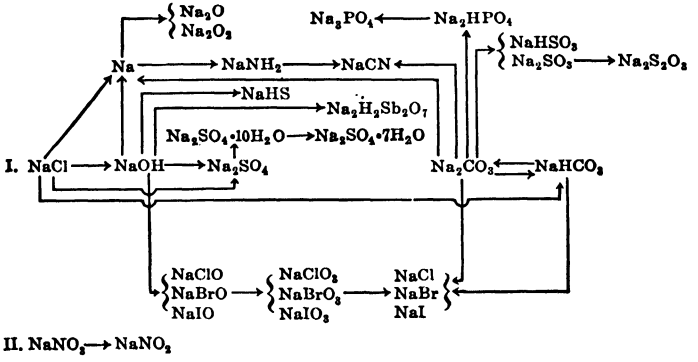


Fig. 17-4. Diagram Showing Steps in the Preparation of Important Compounds of Sodium, Starting with Sodium Chloride or Sodium Nitrate

namely, *sodium bisulfide* (NaHS) and *sodium sulfide* (Na_2S), are well known. *Sodium nitrite* ($NaNO_2$) is formed by heating sodium nitrate with lead; the lead is oxidized to lead oxide (PbO), and thus the nitrate is reduced to nitrite. It is of great use in the preparation of certain compounds of carbon, especially dyes. *Sodium antimonate* ($NaSb(OH)_6$) is the least soluble of all the compounds of sodium. *Sodium chlorate* ($NaClO_3$) is often used as an oxidizing agent. The preparation and properties of *sodium hypochlorite* (NaClO) have been described in an earlier chapter (p. 278).

Potassium and Its Compounds

Occurrence · Potassium is a rather abundant element, being a constituent of many igneous rocks and sea water. Very large deposits of the chloride and sulfate, associated with compounds of calcium and magnesium, occur in the region of Stassfurt, Germany, and are known as *Stassfurt salts*. Similar deposits occur in southern Alsace, France, as well as in many other localities, including Texas and New Mexico, in the United States.

The natural decomposition of rocks containing potassium gives rise to various compounds of the element in all fertile soils. These are necessary for plant growth, so that potassium compounds constitute a valuable fertilizer; this is their chief use.

Stassfurt salts. These salts, evidently deposited from sea water under peculiar geological conditions, form very extensive deposits in middle and northern Germany, the most noted locality for working them being at Stassfurt. The deposits are very thick and rest upon an enormous layer of common salt. They are in the form of a series of strata, each consisting largely of a single mineral salt. Over thirty different minerals are present, but some are in very small quantities. Fig. 17-5 shows a cross section of these deposits. While from a chemical standpoint these strata are salts, they are as solid and hard as many kinds of stone and are mined as stone or coal would be. Since the strata differ in general appearance, they can be mined separately, and each mineral can be worked up by methods adapted to it. The chief minerals of commercial importance in these deposits are the following:

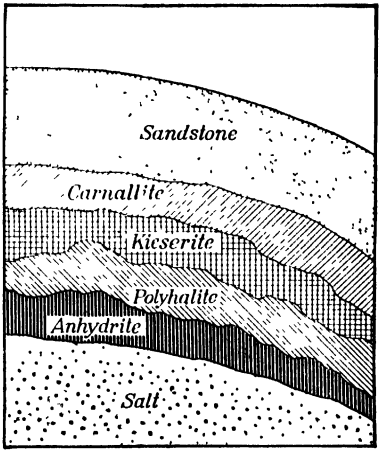


Fig 17-5 Cross-Section Diagram of the Stassfurt Salt Deposits

MINERALS FOUND IN THE STASSFURT SALTS			
Sylvite	KCl	Kieserite	$MgSO_4 \cdot H_2O$
Anhydrite	$CaSO_4$	Schönite	$K_2SO_4 \cdot MgSO_4 \cdot 6\,H_2O$
Carnallite	$KCl \cdot MgCl_2 \cdot 6\,H_2O$	Boracite	$2\,Mg_3B_8O_{15} \cdot MgCl_2$
Halite	$NaCl$	Polyhalite	$MgSO_4 \cdot K_2SO_4 \cdot 2\,CaSO_4 \cdot 2\,H_2O$
Kainite	$MgSO_4 \cdot KCl \cdot 3\,H_2O$		

Sources of potassium salts in the United States. The sources of potassium salts in the United States are the following:

1. Natural brines. Searles Lake, California, is the largest source of potassium compounds from brines. Borax and other sodium salts are also recovered.

2. The ash obtained by burning the waste from molasses fermentation.

3. Alunite, a hydrated sulfate of potassium and aluminum, mined in Nevada and Utah.

4. The ash obtained by burning cottonseed hulls.

5. Potassium-bearing minerals, mined in New Mexico and Texas. Deposits of potassium salts (principally sylvite, polyhalite, and carnallite) have long been known to exist in New Mexico and Texas, but it was not until 1931 that potassium salts from these sources entered the markets of the United States to any extent. These deposits are sufficient to meet all the demands for potassium compounds in the United States.

The Metal · The metal can be obtained by the method used in the preparation of sodium. A more satisfactory method involves the reaction

$$2\,Na + K_2CO_3 \longrightarrow 2\,K + Na_2CO_3$$

Potassium metal has little use, and little of it is produced. It differs from sodium mainly in its greater activity. It decomposes water violently, the heat of the reaction being sufficient to ignite the hydrogen evolved. In general, potassium forms compounds which are similar to the corresponding ones of sodium and therefore will not be discussed in such detail. Very few of them form hydrates.

Potassium Hydroxide (Caustic Potash) (KOH) · This compound is prepared by the methods used in the production of sodium hydroxide. It dissolves in water, forming a strongly basic solution. It is a good dehydrating agent and absorbs water rapidly when exposed to moist air. It is often used in the laboratory to remove both water and carbon dioxide from gases. It is not used to any great extent commercially, because sodium hydroxide is cheaper.

The Potassium Halides · The three compounds potassium chloride (KCl), potassium bromide (KBr), and potassium iodide (KI) are generally referred to as the *potassium halides*. They are very similar in properties to the corresponding sodium compounds. Of these the chloride is the most common, since it is found in quantities in natural deposits. It is obtained not only from *sylvite* (KCl), which is nearly pure potassium chloride, but also from *carnallite* ($KCl \cdot MgCl_2 \cdot 6\ H_2O$). It is used as a fertilizer and in the preparation of nearly all other potassium compounds.

Just as sodium bromide and sodium iodide are prepared by the action of bromine and iodine, respectively, on sodium hydroxide, so the corresponding potassium compounds are prepared by the action of these elements on potassium hydroxide. The reaction in the case of bromine is as follows:

$$3\ Br_2 + 6\ KOH \longrightarrow KBrO_3 + 5\ KBr + 3\ H_2O$$

The potassium bromate ($KBrO_3$) formed is converted into potassium bromide by heating it. Both the iodide and the bromide have a limited use in medicine and in the preparation of salts used in photography.

Potassium Sulfate (K_2SO_4) · This salt is formed by the action of sulfuric acid on potassium chloride. Commercially it is prepared from the Stassfurt salts, especially *schönite* ($K_2SO_4 \cdot MgSO_4 \cdot 6\ H_2O$), by the action of potassium chloride:

$$K_2SO_4 \cdot MgSO_4 + 2\ KCl \longrightarrow 2\ K_2SO_4 + MgCl_2$$

When the solution is evaporated, the resulting potassium sulfate, being much less soluble than the magnesium chloride, separates first. Potassium sulfate is used as a fertilizer and for making potassium aluminum sulfate (potassium alum). When heated with sulfuric acid, it is converted into *potassium bisulfate* ($KHSO_4$).

Potassium Carbonate (Potash) **(K_2CO_3)** · This compound used to be prepared by extraction from wood ashes, and thus acquired the name "potash." It can be prepared from potassium chloride by the Leblanc process, just as sodium carbonate may be prepared from sodium chloride. The Solvay method will not work, since potassium bicarbonate is too soluble and will not separate, as does sodium bicarbonate.

When carbon dioxide is passed into a concentrated solution of potassium carbonate, *potassium bicarbonate* ($KHCO_3$) is formed and, being less soluble than the normal carbonate, precipitates. Both the carbonate and the bicarbonate are very similar to the corresponding compounds of sodium. The chief uses of potassium carbonate are in the manufacture of hard glass and soft soap, and in the preparation of other compounds of potassium.

Commercial preparation of potassium carbonate. Commercially potassium carbonate is usually prepared according to the reactions indicated in the following equations:

$$3\ MgCO_3 + 2\ KCl + CO_2 + H_2O \longrightarrow 2\ MgKH(CO_3)_2\downarrow + MgCl_2 \qquad (8)$$

The resulting carbonate is decomposed when heated:

$$2\ MgKH(CO_3)_2 \longrightarrow 2\ MgCO_3 + K_2CO_3 + CO_2 + H_2O \qquad (9)$$

The magnesium carbonate and carbon dioxide formed according to equation (9) react with a further supply of potassium chloride according to equation (8), and the process thus continues. If equations (8) and (9) are combined, the resulting equation is as follows:

$$MgCO_3 + 2\ KCl \longrightarrow MgCl_2 + K_2CO_3$$

This shows that magnesium carbonate and potassium chloride are the only substances used up in the reaction.

Potassium Nitrate (Saltpeter) **(KNO_3)** · This compound constituted one of the most important reagents of the alchemists. It is formed in the decay of nitrogenous organic matter and therefore accumulates in some regions where the climate is hot and dry. At present it is prepared by the action of sodium nitrate upon potassium chloride:

$$NaNO_3 + KCl \longrightarrow NaCl\downarrow + KNO_3$$

The reaction depends for its success upon the apparently insignificant fact that sodium chloride is almost equally soluble in cold and in hot water. All four compounds represented in the equation are rather soluble in cold water, but in hot water sodium chloride is far less soluble than the other three. When hot saturated solutions of sodium nitrate and potassium chloride are brought together, sodium chloride precipitates, and can be filtered off, leaving potassium nitrate in solution, together with some sodium chloride. When the solution is cooled, potassium nitrate crystallizes out, leaving small amounts of the other salts in solution.

Potassium nitrate dissolves in water with marked absorption of heat. It crystallizes from water in large rhombic crystals, which melt at 333°. When heated alone, it gives up oxygen, forming the nitrite. It was in this way that Scheele first obtained oxygen. It is an excellent oxidizing agent. Its chief use is in the manufacture of gunpowder; for this purpose it is preferable to sodium nitrate, since the latter is deliquescent, and powder made with it, if exposed to air, soon becomes unfit for use. Smaller amounts are used in medicine and as a preservative for meat.

Gunpowder. Black gunpowder is a mixture of potassium nitrate, charcoal, and sulfur. When ignited by a spark it burns explosively, forming a number of products, some of which are gases, while others are solids. The gases constitute about 50 per cent by weight of the total products and consist principally of carbon monoxide, carbon dioxide, and nitrogen, while the principal solids formed are potassium carbonate, potassium sulfate, and potassium sulfide.

Potassium Cyanide (KCN) · Potassium cyanide is very similar to sodium cyanide in its properties. It is extremely poisonous. It is prepared from the compound known as potassium ferrocyanide ($K_4Fe(CN)_6$). When heated to a red heat, potassium ferrocyanide decomposes, forming potassium cyanide, iron carbide, and nitrogen:

$$K_4Fe(CN)_6 \longrightarrow 4\ KCN + FeC_2 + N_2\uparrow$$

With appropriate oxidizing agents, potassium cyanide yields potassium cyanate (KCNO); with sulfur it yields potassium thiocyanate (KCNS). The latter compound serves as a very delicate reagent for the detection of certain compounds of iron; when it is added to solutions of these compounds, the solutions become blood-red in color.

Insoluble Compounds of Potassium · The following compounds of potassium are but slightly soluble in water, so that the metal may be precipitated from its solutions in these forms: (1) *potassium perchlorate* ($KClO_4$), a white crystalline solid; (2) *potassium chloroplatinate* (K_2PtCl_6), a yellow crystalline solid; (3) *potassium sodium cobaltinitrite* ($K_2NaCo(NO_2)_6$), a yellow crystalline solid; (4) *potassium fluosilicate* (K_2SiF_6), a white solid. The solubility of all these compounds is greatly decreased by the addition of alcohol.

Sodium Compounds and Potassium Compounds Compared · The compounds of sodium and potassium so closely resemble each other in properties that, for the great majority of uses, it is immaterial which of the two corresponding compounds is employed. Thus, for an operation requiring a strong base, we may employ either sodium hydroxide or potassium hydroxide. Other things being equal, the cheaper compound will be selected. Since the natural compounds of sodium are much more readily available than those of potassium, we should expect the compounds of sodium to be less expensive and therefore more generally used, and it is true that they are; but it must be remembered that the cost of a compound depends not only upon the availability of raw materials but also upon

the cost of the operation required to produce the compound. Now it is generally true that the salts of sodium are more soluble than those of potassium. Therefore they are often more difficult to obtain in a pure state. For this reason potassium chlorate is more readily obtained pure than sodium chlorate. Again, the compounds of sodium are more deliquescent than those of potassium, and this difference sometimes influences the choice (see gunpowder, p. 302). Sodium salts are usually hydrated, while those of potassium are not. This fact is of importance for some purposes and enters into the cost of shipping.

Rubidium and Cesium

These two elements were discovered by Bunsen while he was making a spectroscopic examination (p. 122) of the residues from certain mineral waters. The characteristic lines in the spectrum of the one are red, while those of the other are blue; hence the names *rubidium*, from a Latin word meaning "red," and *cesium*, from a Latin word meaning "bluish-gray."

Rubidium and cesium are very rare metals. They generally occur together, often associated with potassium and lithium, as in the minerals *carnallite* and *lepidolite*. Cesium also occurs in the form of the rare mineral *pollucite*, a cesium aluminum silicate found on the island of Elba and in New England. Traces of their compounds are found in the soil and are absorbed by certain plants, such as the sugar beet and tobacco. They have also been reported as being present in tea and coffee.

QUESTIONS

1. What are the characteristic properties (*a*) of metals; (*b*) of nonmetals? Give (*c*) six examples of metals; (*d*) six examples of nonmetals.

2. Distinguish between a sodium atom and a sodium ion with respect to (*a*) structure; (*b*) properties; (*c*) reactivity.

3. Show how you can account for the validity of the following statements: *a.* The alkali metals can be expected to be soft, very reactive, and similar in properties, and can be expected to form ions with a charge of + 1. *b.* The ions of the alkali metals should be smaller than their atoms. *c.* The compounds of the alkali metals should be ionic in nature, and highly ionized in solution. *d.* We do not expect to find the alkali metals in the free state in nature. *e.* Cesium can be expected to be more reactive than sodium or potassium.

4. (*a*) Write the equations for the reactions involved in three methods for preparing potassium hydroxide. (*b*) Do any of these methods involve oxidation-reduction reactions?

5. Under what conditions and for what reason will sulfuric acid transform sodium chloride into sodium sulfate?

6. (*a*) Are the salts of potassium or those of sodium more frequently used? (*b*) Name three considerations that determine the choice.

7. Name three of Sir Humphry Davy's important discoveries in chemistry.

8. (*a*) In general, what can be said about the solubility of the common

compounds of the alkali metals? (*b*) How would you account for the fact that compounds of several alkali metals are found in sea water? How do you account for (*c*) deposits of sodium nitrate in the highlands of Chile; (*d*) deposits of alkali metal compounds in salt beds?

9. Write the equations for the reactions that take place in the preparation of the following compounds, using sodium chloride as the source material: (*a*) sodium hydroxide; (*b*) sodium sulfate; (*c*) sodium carbonate; (*d*) sodium sulfite; (*e*) sodium bicarbonate; (*f*) disodium hydrogen phosphate; (*g*) sodium hypochlorite.

10. Give the formula and chemical name of each of the following compounds: (*a*) rock salt; (*b*) hypo; (*c*) soda ash; (*d*) sal soda; (*e*) baking soda; (*f*) saltpeter; (*g*) Chile saltpeter; (*h*) caustic soda; (*i*) caustic potash; (*j*) washing soda; (*k*) Glauber's salt.

11. Write the equations for the reactions that will enable you to bring about the following changes, and state the principle involved in each reaction:

a. $NaCl \longrightarrow Na_2SO_4$ *b.* $NaOH \longrightarrow Na_2SO_3$ *c.* $NaCl \longrightarrow NaHCO_3$
d. $Na_2SO_4 \longrightarrow NaCl$ *e.* $NaCl \longrightarrow NaBr$ *f.* $KNO_3 \longrightarrow KI$

12. What simple tests can be used to identify each of the alkali metals?

PROBLEMS

1. Calculate the per cent of lithium in the mineral spodumene.

2. In making 100 kg of sodium thiosulfate (hypo), what weight of sodium sulfite (anhydrous) is required?

3. A soluble carbonate is required in a reaction to furnish 100 kg of carbonate (CO_3^{--}) ions. If potassium carbonate (anhydrous) costs twice as much as crystallized sodium carbonate ($Na_2CO_3 \cdot 10\ H_2O$), which will be cheaper for the purpose?

4. Suppose 1 g of each of the alkali metals is allowed to react, in a separate beaker, with 100 ml of water. (*a*) Calculate the volume of 0.1 *N* sulfuric acid required to neutralize the basic solution produced in each case. (*b*) Should you expect any difference in the amount of acid required if 200 ml of water were used?

5. (*a*) How many coulombs of electricity will be required to produce 100 g of sodium hydroxide by the electrolysis of a solution of sodium chloride? (*b*) What volume of hydrogen (under standard conditions) will be produced?

6. (*a*) Calculate the weight of limestone, salt, and ammonia necessary for the production of 100 tons of soda ash by the Solvay process if the ammonia and carbon dioxide set free in the series of reactions involved are collected and stored but are not re-used in the process. (*b*) If the recovery of carbon dioxide and ammonia in the above process is 75 per cent efficient, what additional materials and how much of each will be required in order to produce the next 100 tons?

7. A glass company uses 5 tons of anhydrous sodium sulfate daily. If the yield is 90 per cent of the theoretical yield, (*a*) what is the daily consumption of sodium chloride necessary to produce this sulfate? (*b*) what is the yield of hydrogen chloride? (*c*) If the latter were to be dissolved in water to make a solution of density 1.18, containing 36 per cent hydrogen chloride (HCl), what would be the volume of the solution?

CHAPTER 18

CLASSIFICATION OF THE ELEMENTS; THE PERIODIC TABLE

Introduction · In Chapters 16 and 17 it was shown that some of the elements bear marked resemblances to one another and can be grouped into families. Thus, the properties of lithium, sodium, potassium, rubidium, cesium, and francium are very similar, as are the properties of their compounds. The same holds true for the elements fluorine, chlorine, bromine, iodine, and astatine. Moreover, in these families, such differences as exist appear to change in a regular manner with increasing atomic size or weight. Thus, the densities of the alkali metals increase, and the melting points decrease (p. 286), with increasing atomic size. Among the halogen elements similar regularity is observed as one follows the change of a given property from one element to another when the elements are arranged in the order of increasing size of their atoms. Thus, in the series HF, HCl, HBr, and HI the hydrides are increasingly unstable. The boiling points of the free elements increase in the order fluorine, chlorine, bromine, and iodine.

It was only natural that chemists should seek for some basis on which to classify all the elements into such groups. The most desirable basis for such a classification would be some fundamental property possessed by all the elements. For many years it was believed that the logical basis was the relative masses of the atoms, and atomic weights were used originally as the basis for the classification. However, we now know that the *atomic numbers* of the elements are their most fundamental property, even more fundamental than their weights. When the elements are arranged in the order of their increasing atomic numbers, it is found that similar properties recur at regular intervals, and the elements fall naturally into groups. The arrangement thus obtained is called a *periodic table.*

What Is an Atomic Number? The atomic number of an element is the number of positive charges on the nucleus of an atom of that element. This means that the atomic number is the number of protons in the nucleus of the atom (as explained on page 37). The atomic numbers of the elements increase in units of one from 1 for hydrogen, 2 for helium, to 95 for americium, 96 for curium, etc. Every element has its own atomic

number, different from all other atomic numbers; and all atoms which have the same atomic number are atoms of the same element. In fact, the most accurate definition of an element is the following: *An element is a substance all of whose atoms have the same atomic number.*



Fig. 18-1. Wilhelm K. Roentgen (1845–1923) Formerly director of the Physical Institute at Wurzburg, Germany

Experimental Determination of Atomic Numbers · The experimental method by which atomic numbers are determined, involving the measurement of the wave lengths of X rays given off by the elements, was developed by a young Englishman, Moseley (Fig. 18-5). X rays had been discovered by Roentgen (Fig. 18-1) in 1895, and some years later had been shown to be just like visible light rays, only of much shorter wave length. A beam of ordinary white light, when allowed to pass through the prism of a spectroscope (p. 122), is bent, or refracted. The bending is greater for the short waves than for the long waves; and as a result the light is spread out into a spectrum, with the light of short wave length falling at one end of the spectrum and the light of long wave length at the other end. With a spectroscope the wave length of such light can be measured very accurately. However, the X-ray waves are so short that they are not refracted by a glass prism. If their wave lengths are to be measured, it is necessary to find some other method for doing so.

In 1913 Laue had predicted that X rays, falling on a *crystal*, would be reflected or diffracted by the regularly spaced planes of the atoms of the crystal (p. 186). The work that followed his prediction, and the work especially of two English physicists, W. H. Bragg (Fig. 18-2) and W. L. Bragg, father and son, made available a reliable method for measuring the wave lengths of X rays. It was at this point that Moseley, in 1913, began his experimental determinations of atomic numbers.



Fig. 18-2. Sir William Henry Bragg (1862–1942) · He developed X-ray spectrum measurements from crystal reflectors

Moseley's Experiments · The essential feature of Moseley's apparatus was an X-ray tube, a modern form of which was devised by Coolidge (Fig. 18-3) and is known as the Coolidge tube (Fig. 18-4). The glass tube,

T, is highly evacuated. The wire filament, B, generally made of tungsten, is heated by a current from an electric battery to a bright-red heat. At such a temperature some of the electrons in the tungsten atoms escape from the hot filament; and they are driven, like so many bullets, against the target, A,



Fig. 18-3. William D. Coolidge (1873–) The American scientist who invented the most efficient X-ray vacuum tube

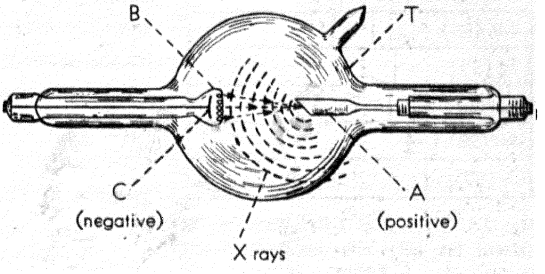


Fig. 18-4. Diagram of a Coolidge X-ray Tube

when the target is connected to the *positive* pole, and the cathode, C, is connected to the negative pole, of a suitable source of direct current of high voltage. The atoms in the surface of the target, under bombardment by electrons, give off X rays. What Moseley did was to use targets made of different metallic elements and to measure, by the method of reflection from crystal planes, the wave lengths of the X rays given off. He found that each one of the different elements gives off X rays of certain wave lengths (a doublet, or pair, of wave lengths, Fig. 18-6), which distinguish the atoms of that element from the atoms of all other elements. All the elements, either in elementary form or in the form of their compounds (with the exception, of course, of the inert-gas elements), have been made into targets and their characteristic wave lengths measured.

Atomic Numbers · If the elements are arranged in a series in the same order as the decreasing wave lengths of their characteristic X rays, the elements are then arranged serially in the order of their increasing atomic number (Fig. 18-6). The serial numbers 1 for H, 2 for He, 3 for Li, 4 for Be, 5 for B, 6 for C, to 92 for U, 93 for Np,



Fig. 18-5. H. G. J. Moseley (1888–1915) He proved that the properties of an atom depend upon its atomic number

94 for Pu, 95 for Am, 96 for Cm, etc., are the atomic numbers of the elements. The beauty of the Moseley method is that it not only allows us to classify the elements in this way, but also makes possible the determination of the number of charges (+) on the nucleus of each atom. *The number of positive charges on the nucleus is the same as the atomic number.* (Although the inert-gas elements cannot be made into targets, and so their atomic numbers cannot be determined in this way, there are blank spaces in the series corresponding to the expected positions of these elements.)

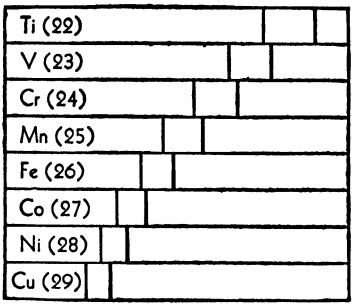


Fig. 18-6. Decrease of X-Ray Wave Lengths (toward the left) with Increasing Atomic Number

Atomic Numbers and the Properties of the Elements · If the elements are arranged in the order of their increasing atomic numbers and the various properties of the elements are examined in the light of this arrangement, it is observed that the properties change in cycles, or periodically. This will be shown in the two following examples:

1. **Atomic number and oxidation state.** If the oxidation states of the elements are examined in the order of increasing atomic numbers, the oxidation states being determined from the formulas of the oxides and

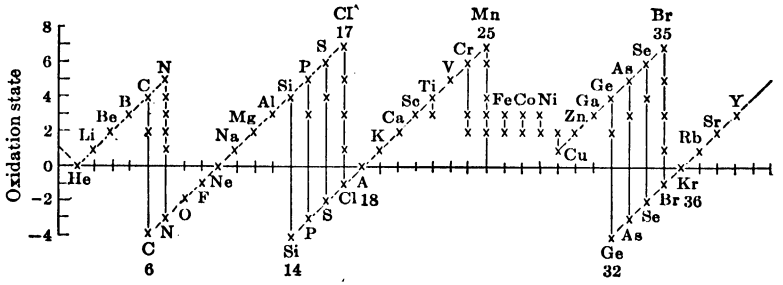


Fig. 18-7. Periodicity in Oxidation State for the Lighter Elements

hydrides and considered arbitrarily as positive in the oxides and negative in the hydrides, an interesting change is observed (Fig. 18-7). Thus, hydrogen has an oxidation state of +1; helium, an oxidation state of 0; lithium, an oxidation state of +1; beryllium, +2; boron, +3; carbon, +4, +2, and −4; nitrogen, +5, +4, +3, +2, and −3; oxygen, −2; fluorine, −1; and neon, 0. Following neon come sodium, +1; magnesium, +2; etc. Note that there is a definite periodicity in the oxidation state.

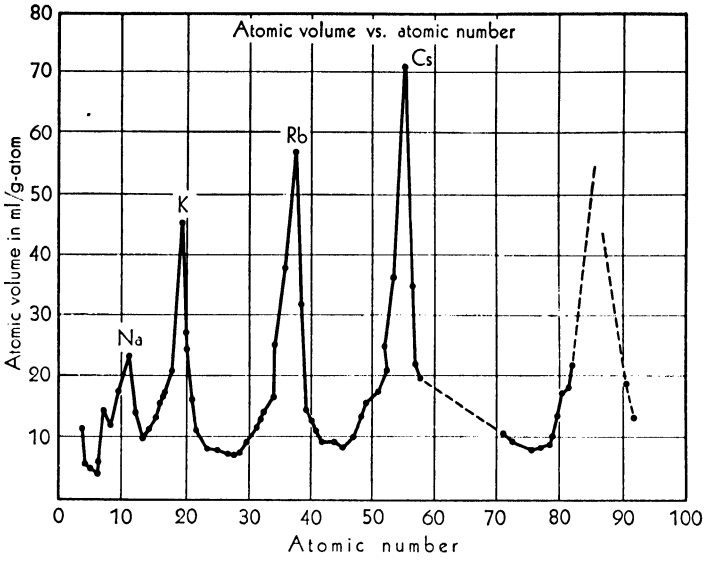


Fig. 18-8. Periodicity in Atomic Volume for the Elements

2. **Atomic number and atomic volume.** If atomic volume (volume occupied by 1 g-at. wt of the free element as a solid or a liquid) is plotted against atomic number, one obtains a periodicity (Fig. 18-8) which resembles that for the oxidation state (Fig. 18-7).

The Periodic Law · Many other properties of the elements and their compounds have been plotted against atomic numbers, and periodicities of the properties have been found. These many facts are summarized in the great generalization known as the *periodic law*: *The physical and chemical properties of the elements are periodic functions of their atomic numbers.* In other words, if the elements are arranged in the order of their increasing atomic numbers, the variation of the properties of the elements follows a recurring cycle, much like that of the seasons. The usefulness of the periodic law is not that of a mathematical equation but is rather of qualitative and suggestive character.

Periodic Table—General Plan of Arrangement · The periodic relationships may often be clearly shown by graphs like those of Figs. 18-7 and 18-8, but may also be shown to great advantage by a properly arranged table, or *periodic table.* Many different periodic tables have been suggested, but a somewhat modified form of the original table that was proposed by the Russian chemist Mendeleev (Fig. 18-9) in 1869 is very commonly used.

If hydrogen is omitted, the next eight elements all differ markedly from one another in both chemical and physical properties, and these

eight elements arranged in the order of their increasing atomic numbers constitute a first period, as follows:

2	3	4	5	6	7	8	9
He	Li	Be	B	C	N	O	F

The tenth element, neon, is very similar to helium. Placed just below the latter, it starts a second period:

10	11	12	13	14	15	16	17
Ne	Na	Mg	Al	Si	P	S	Cl

The next element, argon, resembles neon, and begins a third period:

18	19	20	
A	K	Ca	etc., as given in the periodic table (p. 311).

An inspection of the elements in the eight *vertical* columns (or *groups*) brings to light a remarkable fact. Not only are helium, neon, and argon very similar, but a more or less pronounced resemblance is found among the several elements in each of the columns. Thus, lithium, sodium, and potassium are very similar, as are beryllium, magnesium, and calcium.

Short and Long Periods · The first two periods, just described, are *short* periods. The first short period, from helium to fluorine, contains eight elements; and the second short period, from neon to chlorine, also contains eight elements. In the third period, a *long* period, from argon to bromine, there are eighteen elements; and there are also eighteen elements, from krypton to iodine, in the fourth period, which is also a long one. If these two long periods are to be compressed into the vertical columns, or groups, of a table of this type, it is necessary to spread each of them over two rows. In order not to interrupt the regularities of the third period, the three elements following manganese,—namely, iron, cobalt, and nickel,—which resemble one another very closely, are set aside in a separate ninth column; and similarly, in the fourth period, the three elements following technetium are placed in the ninth column.

The next period (fifth), a *very long* period, consisting of thirty-two elements, extending from xenon to astatine, also contains three elements—osmium, iridium, and platinum—in the ninth column, and resembles the two previous long periods with the exception that there are fifteen *rare-earth elements* (atomic numbers, 57–71) in Group III, instead of a single element. This apparently anomalous situation, however, is in strict accord with chemical behavior because all the rare-earth elements resemble one another so closely that their separation is extremely difficult. The final period (sixth), which starts with radon, and which also contains a group of closely related elements, called the *actinide series*, is incomplete.

Two Families in a Group · A study of the elements within a group discloses a further fact of much interest. As we have seen, the relation-

A MODERN FORM OF THE MENDELEEV PERIODIC TABLE

Type of Hydride		RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH	
Type of Oxide		R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
Period	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
0		1.008 H							
1	4.003 He	6.940 Li	9.013 Be	10.82 B	12.01 C	14.008 N	16.000 O	19.00 F	
2	20.183 Ne	22.997 Na	24.32 Mg	26.97 Al	28.06 Si	30.98 P	32.066 S	35.457 Cl	
3	39.944 A	A 39.096 K / B 63.54 Cu	A 40.08 Ca / B 65.38 Zn	A 45.10 Sc / B 69.72 Ga	A 47.90 Ti / B 72.60 Ge	A 50.95 V / B 74.91 As	A 52.01 Cr / B 78.96 Se	A 54.93 Mn / B 79.916 Br	55.85 Fe, 58.94 Co, 58.69 Ni
4	83.7 Kr	85.48 Rb / 107.880 Ag	87.63 Sr / 112.41 Cd	88.92 Y / 114.76 In	91.22 Zr / 118.70 Sn	92.91 Nb / 121.76 Sb	95.95 Mo / 127.61 Te	99 Tc / 126.92 I	101.7 Ru, 102.91 Rh, 106.7 Pd
5	131.3 Xe	132.91 Cs / 197.2 Au	137.36 Ba / 200.61 Hg	Rare-Earth Elements / 204.39 Tl	178.6 Hf / 207.21 Pb	180.88 Ta / 209.00 Bi	183.92 W / 210 Po	186.31 Re / 210 At	190.2 Os, 193.1 Ir, 195.23 Pt
6	222. Rn	223 Fr	226.05 Ra	Actinide Series					

Rare-Earth Elements	138.92 La	140.13 Ce	140.92 Pr	144.27 Nd	147 Pm	150.43 Sm	152.0 Eu	156.9 Gd	159.2 Tb	162.46 Dy	164.94 Ho	167.2 Er	169.4 Tm	173.04 Yb	174.99 Lu
Actinide Series	227 Ac	232.12 Th	231 Pa	238.07 U	237 Np	239 Pu	243 Am	243 Cm	245 Bk	246 Cf	255 E	255 Fm	256 Mv		

ship between the corresponding elements in Periods 1 and 2 is a very close one. Below this point the elements in each group (except in Groups 0 and VIII) fall very naturally into two subgroups, called *families*. In the table these are designated *A* and *B*. The elements in one family resemble one another much more closely than they do those in the other family in the same group. Thus, in Group II, calcium, strontium, barium, and radium form one family of very similar elements, while zinc, cadmium, and mercury constitute the other.

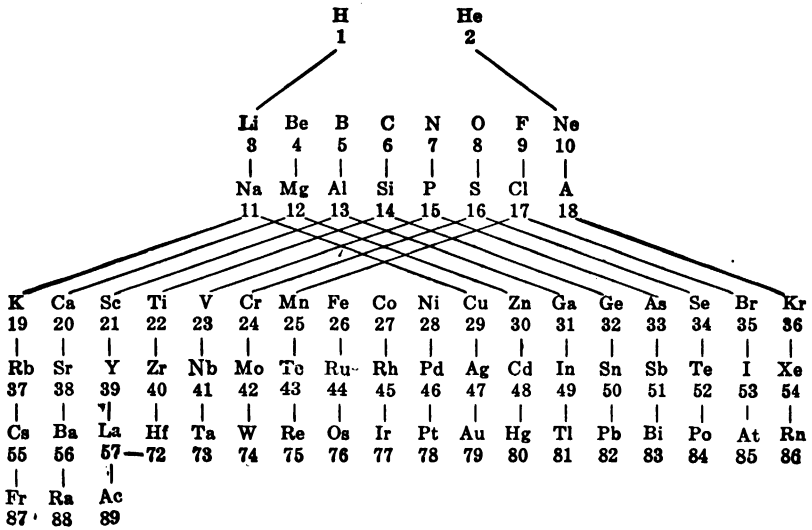
Group Resemblances · In any one group the elements have much the same characteristics. They may therefore be expected to form oxides, hydroxides, acids, and salts of the same general formula. The hydrides

and oxides of *maximum* oxidation state are indicated by the formulas at the top of the columns (p. 311). It will be seen that the positive oxidation state increases from 0 in Group 0 to 8 in Group VIII, while that toward hydrogen reaches a maximum in Group IV. For example, sulfur, in the sixth column, has an oxidation state of + 6, as shown in the oxide of the formula SO_3, while its oxidation state in the compound H_2S is − 2. It usually happens that, in addition to the oxide characteristic of a group, each element forms other oxides not predicted by the table — for example, sulfur dioxide (SO_2).

Family Resemblances · The resemblances of the members of a family to one another are more marked and extend not only to the general chemical characteristics, but to physical properties as well. There is, in most cases, a more or less regular variation in any given property as we pass from the member of smallest atomic number to that of largest, the middle ones are intermediate to the others. This is true in regard to chemical activity and such properties as melting point, boiling point, density, color, solubility of analogous salts, and many similar properties. These points will be dwelt upon as the families are taken up in order.

Other Forms of the Periodic Table · Various other tables have been devised in an attempt to show somewhat more satisfactorily the relationships that are found when family *A* and family *B* of a group are compared. One of these is the Thomsen table (shown below) and another is the extended form shown on page 313.

THOMSEN'S TABLE OF THE ELEMENTS



QUESTIONS

1. (*a*) Explain what is meant by a "periodic" process. Mention (*b*) six periodic processes in nature; (*c*) six in mechanics or machinery.

2. Construct the periodic table from memory to the extent of placing 20 to 30 elements.

3. Astatine (at. no., 85) has been produced artificially. From your knowledge of the chlorine family predict (*a*) the physical state and color of the free element; (*b*) the relative stability and acidity of its hydride; (*c*) the solubility of its compound with sodium; (*d*) the formula of its hydride; (*e*) the compound it would form with calcium.

4. (*a*) What would be the formula for radium (Ra) chloride? (*b*) Consult a chemical handbook for the solubilities of calcium sulfate ($CaSO_4$), strontium sulfate ($SrSO_4$), and barium sulfate ($BaSO_4$), and state what you would expect the solubility of radium sulfate ($RaSO_4$) to be.

5. (*a*) The element antimony (at. no., 51) will most nearly resemble which of the following elements: tin (at. no., 50), tellurium (at. no., 52), niobium (at. no., 41), tantalum (at. no., 73), or arsenic (at. no., 33)? (*b*) Give reasons for your answer in terms of the periodic table. (*c*) Which form of the periodic table shows this relationship most clearly?

6. Pick out four other sets of "triads" similar to those of Döbereiner.

7. Account for the fact that the atomic weights of the elements tellurium and iodine are not in the same order as their atomic numbers.

8. A list of the melting points of some of the elements may be found in the Appendix. Plot these melting points on co-ordinate paper, against the atomic numbers of the elements. What can you say about your results?

CHAPTER 19

THE STRUCTURE OF THE ATOM

Introduction · In Chapter 4 we presented briefly (pages 36–39) some of the essential features of the theory of atomic structure. We should now consider the evidence on which the theory is based. Some of this evidence has already been developed. Isotopes have been discussed in Chapter 9, and the determination of their weights and relative amounts by means of the mass spectrometer has been described. Further, we have learned, in the preceding chapter, how the atomic number, or number of positive charges on the nucleus of an atom, can be found by the Moseley method. We learned also (Chap. 4) of the discovery that electrons can be obtained from all forms of matter, and that protons and neutrons are also present in all varieties of matter (except that hydrogen atoms contain no neutrons). In this chapter we shall show how the discovery of radium by Marie and Pierre Curie, the brilliant experimental work and deductive reasoning of Lord Rutherford and his associates, and the discoveries made through spectroscopic observations and measurements of ionization potentials, have been combined with the facts of the periodic behavior of the elements into a theory of atomic structure embracing not only the nucleus but the outer regions of the atom. This theory enables us to explain not only the behavior of the elements but also the physical and chemical properties of their compounds.

1. EVIDENCE FROM RADIOACTIVITY

In the year 1896 the French physicist Becquerel (Fig. 19-1) discovered that the element uranium, as well as its compounds, gave off a kind of emanation or rays which would affect photographic plates or discharge an electroscope. This emanation was given off continuously, with no apparent diminution on standing. The phenomenon has come to be called *radioactivity*. Becquerel developed methods of measuring the amount of radiation given off, and showed that the radioactivity was directly proportional to the amount of uranium present in the sample tested. There was, however, one important exception. The mineral *pitchblende*, a uranium ore, was about four times as radioactive as could be accounted for by the amount of uranium in the ore. He discussed this discrepancy with his friend Marie Curie (Fig. 19-2), and they decided that

there must be some other element present more radioactive than uranium. Madame Curie and her husband agreed to try to isolate this unknown element. They obtained several tons of pitchblende (donated by the

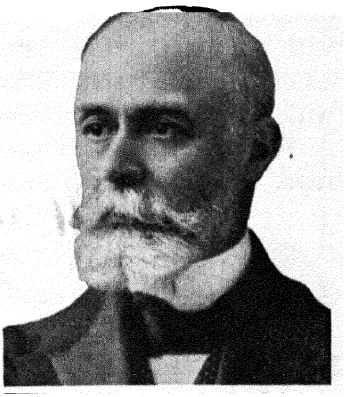


Fig. 19-1. Antoine Henri Becquerel (1852–1908) · French physicist Professor of physics in the laboratory of the National Museum of Natural History in Paris He made many discoveries in the field of optics In 1896 he discovered that radiographs could be produced by uranium salts similar to those produced by X rays It was this discovery that suggested to Monsieur and Madame Curie the investigations that later led to the discovery of radium and polonium In 1903 the Nobel prize for physics was divided between Monsieur Becquerel and Monsieur and Madame Curie

Austrian government) and started the laborious task of separating this unknown element. By gradually concentrating the more radioactive portions, by repeated chemical fractionation, they were finally able, in July of 1898, to collect a tiny amount of the sulfide of a new element, which they called *polonium* in honor of Marie's native Poland. In December of the same year they isolated a small amount of another element, radium, in the form of radium sulfate, $RaSO_4$. Both of the new elements, polonium and radium, were found to be far more radioactive than uranium. In fact, radium proved to be so radioactive that its salts would glow in the dark, and exposure to the rays would cause a severe burn.

Among the scientists whose interest was aroused by this work was Ernest Rutherford, a New Zealander associated with J. J. Thomson in the Cavendish laboratory in Cambridge, England. In a remarkable



Bettmann Archive

Fig. 19-2. Madame Marie Curie (1867–1934) · Professor in the Sorbonne, Paris Born in Warsaw, Poland, Madame Curie, together with her husband, Pierre Curie, discovered polonium in July, 1898, and radium in December, 1898. Monsieur Curie was killed in a street accident in 1906 Madame Curie continued the investigations, isolating pure radium, studying its properties, and determining its atomic weight. Recipient of the Nobel prize for chemistry, 1911. Elected honorary member of the American Chemical Society in 1909

series of experiments, some carried out at Cambridge, some at McGill University in Montreal, Rutherford and his associates showed that radioactivity resulted from a disintegration of atoms, or, rather, a series of disintegrations, in which elements were transmuted into other elements, with the evolution of enormous amounts of energy in proportion to the amounts of matter undergoing change. His first experiments had to do with the nature and properties of the rays.

The Nature and Properties of the Rays · **1. Alpha, beta, and gamma rays.** In a very simple experiment Rutherford (Fig. 19-6) showed that there were three kinds of rays, which he named alpha (α), beta (β), and gamma (γ) rays. He placed a small quantity of a material containing radium at the bottom of a hole bored in a piece of lead (Fig. 19-3). All rays were stopped, by the shielding power of the lead, except those headed directly upward. He then placed the radium between the poles of a magnet, as shown, with a photographic plate (protected from light) arranged above to receive the rays. The alpha rays were bent to the extent and in the direction that one would expect (pp. 36, 144) for relatively heavy, positively charged particles passing through a magnetic field; and further study proved them to be helium nuclei, He^{++}. The beta rays, deflected in the opposite direction and to a much greater extent, behaved like negatively charged particles of very small mass; they are electrons (p. 36). The gamma rays, not deflected at all, are waves of light, like X rays (p. 307) but of shorter wave length.

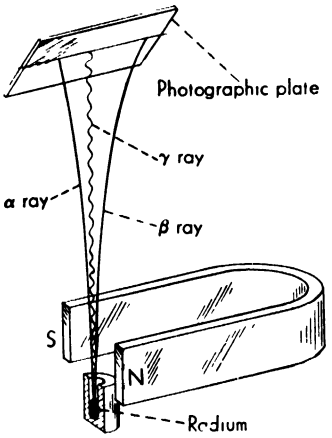


Fig. 19-3. Magnetic Deflection of Rays · Gamma rays are not bent, but alpha and beta rays are bent to the left and to the right, respectively, in a magnetic field, as shown

2. Speed of travel of the rays. The velocity of the gamma rays is the same as that of light, 3×10^{10} cm/sec, or 186,000 miles/sec. The velocity of the alpha particles depends on the kind of nucleus from which they are ejected, but ranges from 9000 to 14,000 miles/sec. And the beta particles often travel as fast as 100,000 miles/sec, and when ejected from radium C, as fast as 98 per cent of the velocity of light.

3. Penetrating power of the rays. The alpha particles cannot penetrate any except the thinnest sheets of metal, and are stopped even by an ordinary piece of paper. The beta particles have greater penetrating power than the alpha particles, but are stopped by relatively thin sheets of metal. The gamma rays can penetrate thick layers of metal, and can

be detected after traversing 8 or 10 in. of lead. The relative penetrating power of the three types of particles, tested toward aluminum, are approximately as follows: alpha particles, 1; beta particles, 100; gamma rays, 10,000.

4. **Ionizing power of the rays.** As they pass through air or other gases, all three kinds of rays have the power to *ionize* gas molecules by knocking out electrons from the outer regions of the atoms of which the molecules are composed. Gas or air in the neighborhood of a radioactive substance is thus made electrically conducting, and it is for this reason that an electric charge placed on an electroscope gradually leaks off.

A diagram of an electroscope is shown in Fig. 19-4. An electric charge, say from a hard-rubber rod that has been rubbed with a woolen cloth, is introduced onto $Plate_1$. This charge spreads down the supporting metal rod to a flat metal strip and to a leaf of gold foil or aluminum foil, and the leaf is repelled across the scale to a steady position. Now, if a radioactive material is brought near $Plate_1$, as at C, the air between $Plate_1$ and $Plate_2$ becomes conducting, because of the ions formed, and the charge leaks across the air gap to $Plate_2$ and thence to the earth. The leaf falls back to its original (vertical) hanging position. The rate at which the leaf falls is a measure of the intensity of the ionizing rays. Electroscopes (or electrometers) of this sort have been much used, not only to show the presence of radioactive substances but also to measure the intensity of the radioactivity.

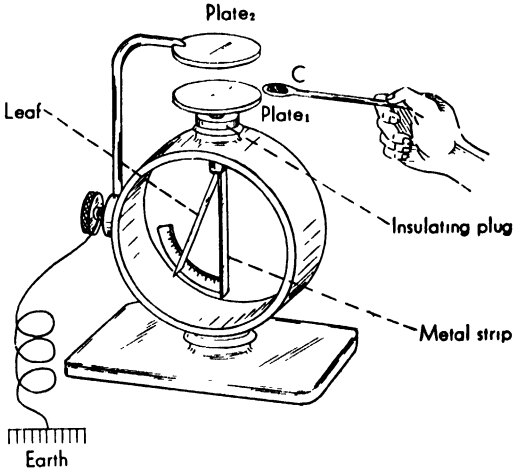


Fig. 19-4. Discharge of an Electroscope by Ionizing Rays from a Radioactive Material

Radioactivity a Series of Decompositions · It is not to be thought that the atoms of uranium or radium explode into alpha, beta, and gamma rays and nothing else. Rather, the atom gives off an alpha or beta particle from its nucleus, forming thereby the nucleus of a new kind of atom. Sometimes a gamma ray is evolved as one or the other of the nuclei lose energy in changing to a more stable atom. The new atom may in turn evolve a beta or alpha particle, changing to a third atom, and so on, giving rise to a series of changes, in each of which one or more kinds of

these rays are given out, and a new kind of atom is formed. These changes cease when they result in a new atom that is stable and not radioactive. The atoms of the element uranium are the starting point in this series of changes, and those of radium are among the most stable (slowest to change) of all atoms in the series.

The Uranium Disintegration Series · There are several isotopes of uranium, but it is the isotope of mass 238, usually designated as uranium I (UI), that is the starting point in the uranium series of radioactive changes, as shown in the table below.

Beginning with uranium I, disintegration proceeds by successive steps, passing through uranium X_1 to uranium X_2, and so on to the final product, lead, with radium as one of the intermediate products. Such a series is known as a disintegration series, and reminds one of the generations in human life—great-grandmother, grandmother, mother, daughter. Uranium I, then, is the great-great-great-grandmother of radium, and the original ancestor in the whole radium lineage.

URANIUM DISINTEGRATION SERIES

NAME	SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	ISOTOPE	RADIATION	HALF-LIFE
Uranium I . .	U I	238	92	U	α	4.51×10^9 yr
Uranium X_1 . .	U X_1	234	90	Th	β, γ	24.5 days
Uranium X_2 . .	U X_2	234	91	Pa	β, γ	1.14 min
Uranium II . .	U II	234	92	U	α	2.69×10^5 yr
Ionium	Io	230	90	Th	α, γ	8.3×10^4 yr
Radium	Ra	226	88	Ra	α, γ	1590 yr
Radon	Rn	222	86	Rn	α	3.825 days
Radium A . . .	Ra A	218	84	Po	α	3.05 min
Radium B . .	Ra B	214	82	Pb	β, γ	26.8 min
Radium C . .	Ra C	214	83	Bi	α, β, γ	19.7 min
Radium C′ . .	Ra C′	214	84	Po	α	1.5×10^{-4} sec
Radium C″ . .	Ra C″	210	81	Tl	β	1.32 min
Radium D . .	Ra D	210	82	Pb	β, γ	22 yr
Radium E . .	Ra E	210	83	Bi	β	5 days
Radium F . . .	Ra F	210	84	Po	α, γ	140 days
Radium G (lead)	Ra G	206	82	Pb		Infinite

Some of the transformations take place very rapidly, others slowly; but the rate seems not at all affected by external conditions, such as temperature (no matter how high or low). It is convenient to state the rate of change in terms of the half-life, that is, the time required for half of any given weight of the element to change. The more rapid the decay, the greater is the energy with which the rays are emitted. The kinetic energy of the rays may appear as heat. For instance, 1 g of radium hourly

evolves about 134 cal of heat. The total heat given off in a calorimeter by the complete disintegration of 1 g of radium would be something like 350,000 times the heat of combustion of 1 g of carbon.

Radioactive Elements and the Periodic Table · Fig. 19-5 shows the position of the members of the uranium disintegration series in the periodic table. The loss of one alpha particle, He^{++}, by the nucleus of an atom results in a lowering of the atomic weight by 4 units; a lowering of the positive charge on the nucleus, and hence a lowering of the atomic number, by 2 units; and a shift to the left in the table of two places. With beta-particle emission there is no change in atomic weight, but there is a gain of 1 in the atomic number and a shift to the right of one place. The changes in atomic weight are indicated vertically.

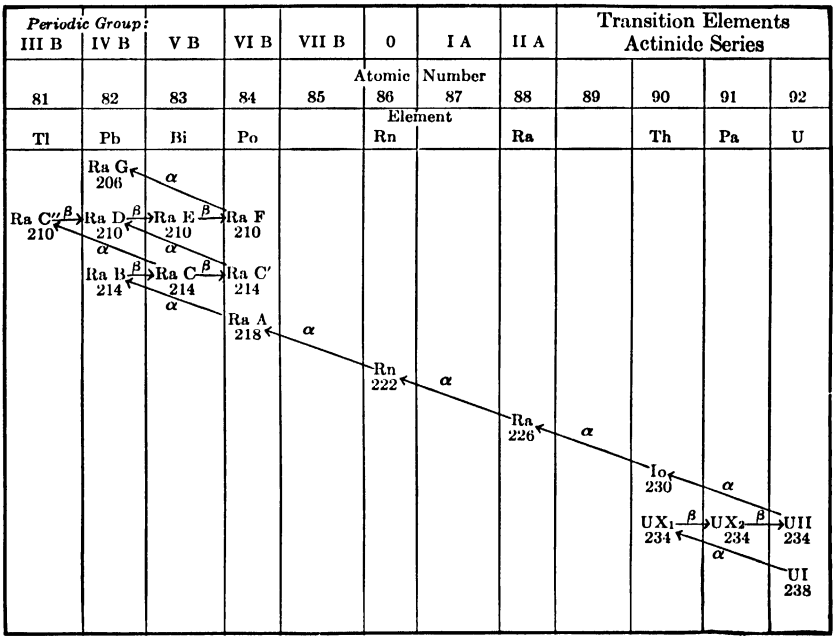


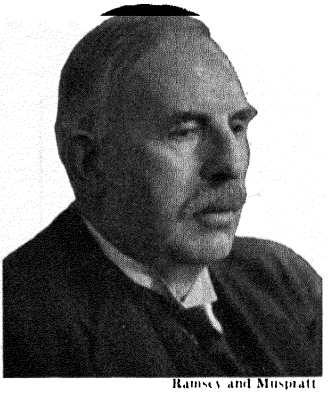
Fig. 19-5. The Uranium Series in the Periodic Table

Note that the vertical columns in Fig. 19-5 correspond to separate places in the periodic table, and that two or more atoms occupying the same place are isotopes. For example, Ra B, Ra D, and Ra G are all isotopes of lead, with the same chemical properties, although, of course, the first two are radioactive and ordinary lead is not. (Indeed, native specimens of lead that have probably originated from the disintegration of uranium are found to have atomic weights different from ordinary

lead.) There are a great many radioactive isotopes. Thorium and actinium (and neptunium), like uranium, form disintegration series of their own; and many of the members of those two series are isotopes of members of the uranium series.

2. INFORMATION OBTAINED BY BOMBARDMENT WITH ALPHA PARTICLES

Rutherford's Experiments · Having shown that atoms are not indestructible units but have, themselves, a structure, Rutherford next tackled the problem of finding out what that structure is. In the short space of two years after the discovery of radium Sir J. J. Thomson (Fig. 4-2) had shown that electrons are an integral part of the structure of all atoms. Since atoms themselves are neutral it would seem that they must have a positively charged portion to balance the negative charge of the electrons. Rutherford showed this to be the case, and located this positive part by some very ingenious experiments.



Ramsey and Muspratt

Fig 19-6. Lord Rutherford (1871–1937) Director of the Cavendish Laboratory, Cambridge, England

Suppose that we were shooting at a target of rather large area with a machine gun, and that we scattered the fire all over the target. If now we were to take some small cannon balls, the size of large oranges, and pile them together as in Fig. 11-23 or Fig. 11-29 (pp. 184, 188), in front of the target and in the line of fire, certainly no bullets would be able to penetrate the pile and hit the target. They would bounce off the cannon balls. Rutherford (Fig. 19-6) performed essentially this same experiment with atoms. He directed a stream of atom-sized bullets (alpha particles) at a photographic plate or at a fluorescent screen, so that the spots where the alpha particles struck the target could be observed. Then he introduced into the line of fire, in front of the target, a piece of gold foil, the atoms of which are piled together compactly, just as the cannon balls are, in the face-centered cubic piling (Figs. 11-23, 11-29). In Rutherford's experiment most of the alpha particles went through the gold foil, which was at least several hundred atoms thick. However, some of the



Science Service

Fig. 19-7. Niels Bohr (1885–) Professor of theoretical physics, University of Copenhagen, and author of the Bohr theory

particles were deflected from a straight path and were caused to veer off at sharp angles, and occasionally (a few in many thousand) were repelled backward. Similar results were obtained with other metals.

Interpretation of Rutherford's Results · The results of these alpha-particle experiments suggested to Rutherford that gold atoms are not hard, solid spheres, but are extremely open and porous in their structure. The alpha particles, traveling with terrific velocity, go directly through the atoms themselves, perhaps with the same relative ease with which the machine-gun bullets would cut through a pile of oranges instead of cannon balls. The only satisfactory suggestion which Rutherford could make to explain the deflection and repulsion of alpha particles was to suppose that *practically all the mass of the atom is concentrated at the center, in a positively charged nucleus*. The strong positive charge of the nucleus deflects or repels any positively charged alpha particle which in its flight through the metal atoms happens to pass close to a nucleus (Fig. 19-8). The nucleus is hard and dense, and is very small (diameter about 10^{-12} cm) compared with the whole atom (diameter about 10^{-8} cm). The electrons patrol the outer domain of the atom, and guard it against invasion by other atoms.

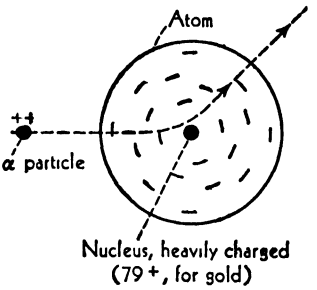


Fig. 19-8. Diagram Showing an Alpha Particle Passing through a Gold Atom

Rutherford, from his study of the exact angles of deflection of those alpha particles which were caused to deviate from a straight line, was able to calculate with fair accuracy the actual charge on the nucleus of the gold atom (and other atoms). A more accurate determination of the number of positive charges on the nucleus results from the Moseley method, as described below.

3. INFORMATION OBTAINED BY BOMBARDMENT WITH ELECTRONS

Moseley's Experiments and the Charge on the Nucleus · We have already described Moseley's experiment (p. 306) with an X-ray tube, in which the target is bombarded by electrons shot out from the cathode. The target may be made of any one of various elements or their compounds. The atoms in the surface of the target are subjected to the electron bombardment, and under this bombardment the atoms emit X rays.

In all atoms (except hydrogen) there are two electrons which are *very close* to the nucleus (as we shall see later). The disturbance of these two

electrons by the bombarding bullet electrons results in the emission of X rays. When the nucleus of the atom carries a large positive charge, these two electrons are bound very tightly to it, and the X-ray wave length is short; in other atoms, of smaller nuclear charge, the binding is not so tight, and a longer wave is given out. Thus the very fact that the X-ray wave lengths *decrease* regularly in stepwise fashion as we go up the atomic-number series (Fig. 18-6) means that the nuclear charges also *increase* regularly in a stepwise fashion, 3, 4, 5, 6, 7. *The number of positive charges on the nucleus of an atom is the same as the atomic number of the atom* (p. 307).

Tentative Theory of Nuclear Structure · Any theory of the structure of the nucleus of the atom must account not only for the positive electric charge on the nucleus but also for the mass of the atom, since this is almost entirely concentrated in the nucleus. It is reasonable to suppose that the charge is due to protons (mass 1, charge + 1). However, protons alone will not account for the mass of the atoms, which (except in the case of the hydrogen atom) is two or more times as large as the number of protons (positive charges). The rest of the mass is contributed by the neutrons (mass 1, charge 0), which do not add to the charge. The nuclei of the first ten elements in the periodic table are shown in Fig. 19-9, in which protons and neutrons are designated by the letters "p" and "n" respectively. (Compare this discussion with that on page 37.)

	H	He	Li	Be	B	C	N	O	F	Ne
	1p	2p 2n	3p 4n	4p 5n	5p 6n	6p 6n	7p 7n	8p 8n	9p 10n	10p 10n
Charge on nucleus	1+	2+	3+	4+	5+	6+	7+	8+	9+	10+
Resulting atomic mass	1	4	7	9	11	12	14	16	19	20

Fig. 19-9. Nuclei of the First Ten Atoms

Our picture accounts not only for atomic numbers (number of positive charges) but also approximately for atomic weights. It is in line with the results of Rutherford's experiments, which show that most of an atom's mass is concentrated in the nucleus, for we have placed the two massive components of the atoms, the protons and neutrons, in the nucleus. Indeed, this tentative theory is already very close to the truth; and with a few further modifications, we may say that it represents substantially the views of modern physicists about the composition of atomic nuclei.

4. INFORMATION OBTAINED FROM A STUDY OF ISOTOPES

Nuclei of Isotopes · In a previous chapter (p. 144) we saw that *isotopes* are atoms having the same atomic number and chemical characteristics but different atomic masses (mass numbers), and that it is in terms of *mixtures of isotopes* that we account for fractional atomic weights. How do the atomic nuclei of the isotopes differ from one another?

To answer this question, let us take the case of lithium. It has been demonstrated experimentally by the mass spectrometer that some lithium atoms have a mass number of 6 and others of 7. If we took a lithium atom of mass number 6, with a nucleus of the composition shown in Fig. 19-10, *A*, and introduced into the nucleus another neutron, Fig. 19-10, *B*, we should increase the mass number to 7 without disturbing the nuclear charge (which is 3 + in each case). Neutrons would not change the arrangement of the electrons in the outer region of the atoms, and hence would not affect the *chemical* properties of the atom (p. 37). The two principal chlorine isotopes would have nuclei of the composition shown in Fig. 19-11, *A* and *B*.

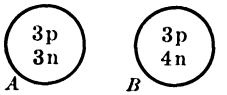


Fig. 19-10. Nuclei of Isotopes of Lithium

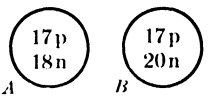


Fig. 19-11. Nuclei of Isotopes of Chlorine

The Electrons in the Atom

Evidence for the Distribution of the Electrons · Let us now turn our attention to the arrangement of the electrons which circulate in the outer region of the atom. We may discuss four lines of evidence which are helpful in forming a theory about the positions of the electrons: (1) evidence from spectroscopic behavior, (2) evidence from periodic relationships, (3) evidence from ionization potentials, and (4) evidence from the facts of chemical combination.

1. EVIDENCE FROM SPECTROSCOPIC BEHAVIOR

In Chapter 8 reference was made to the spectra of helium and the other rare gases of the atmosphere. From the pattern of the lines in the spectrum of an element it is possible to deduce the various energy levels of the electrons in the outer region of the atom. The manner of making this deduction will be exemplified by the following study of the spectrum of hydrogen.

The Spectrum of the Hydrogen Atom · If hydrogen gas is introduced, at low pressure, into a Plücker tube (Fig. 8-15, p. 123) and excited by the electric discharge from an induction coil, some of the molecules are split into atoms; and these atoms glow, or give off light which may be examined spectroscopically. The spectrum is not continuous, but is a series of colored lines of the type shown in the color plate facing page 122. The first line, of longest wave length, is red, the second blue, the third violet, the fourth very close to the ultraviolet, and the rest are in the ultraviolet region. A look at the spectrum of hydrogen (Fig. 19-12) shows that the wave lengths of the lines appear to have some sort of mathematical relationship to each other, the distances apart decreasing with decreasing wave length, and also decreasing in intensity. The significance of this fact will appear later.

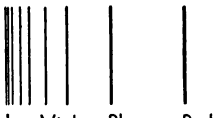


Fig. 19-12. Spectrum of Hydrogen

The Bohr Theory · We have very good reasons for believing that the single electron, in the space surrounding the nucleus of the hydrogen atom, is responsible for the production of these spectral lines. According to the theory suggested by Niels Bohr (Fig. 19-7), the hydrogen atom is something like a solar system, with only one planet (the electron) revolving about a sun (the single proton of the nucleus). The electron is supposed to be able to move in a number of different shells, or in different energy levels, *K*, *L*, *M*, *N*, *O*, as shown in Fig. 19-13. Bohr supposed

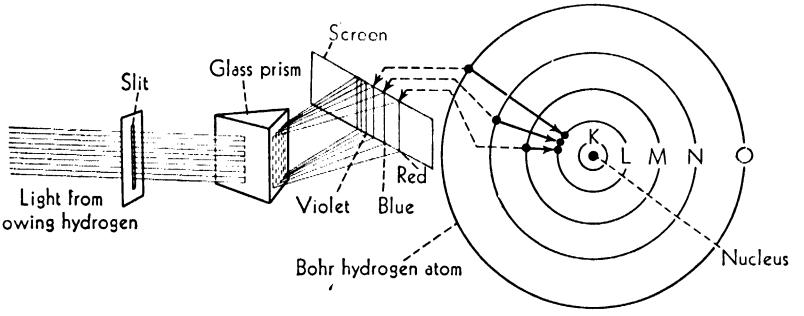


Fig. 19-13. Diagram Showing the Relation between the Wave Length of Light and the Fall of the Electron in the Hydrogen Atom, as Interpreted by the Bohr Theory

that the electron can revolve only in these fixed shells, and not in other orbits between them, as though the shells were fixed tracks in space. In the usual hydrogen atom, in its normal state, the electron is in the *K* level. But the hydrogen atom can be made to absorb energy, under electron bombardment in the Plücker tube or by illumination with light

of a suitable sort, and the electron can thus be lifted to a higher level, *L*, *M*, *N*, or *O*; or it can be lifted entirely out of the atom, in which case the atom becomes ionized (H^+). As soon as the excitation of the hydrogen ceases, the electrons start to fall back again from the higher energy levels to the lower energy levels, that is, from the outer to the inner levels. The energy released by these falls is emitted by the atom as light; and the greater the energy of fall, the shorter the wave length of the light, as shown in the atom diagram in Fig. 19-13.

The situation reminds us of an elevator, if we suppose that by automatic control the elevator car can stop only at the floor levels, not between floors. The elevator, normally waiting for passengers on the ground level, can, by the absorption of energy, be lifted to any floor above; then, when it falls back to lower floors, energy is released- the greater the fall, the greater the energy released.

Since the energy required to lift an electron from an inner to an outer shell is exerted to overcome the attraction of the positively charged nucleus, the energy used in moving the electron from the *K* shell to the *L* shell is greater than that required to move it from the *L* shell to the *M* shell, and so on. These energy relationships are pictured in Fig. 19-14. The analogy between this relationship and the lines in the spectrum of hydrogen shows how the wave lengths of light may be used to locate the electrons in shells.

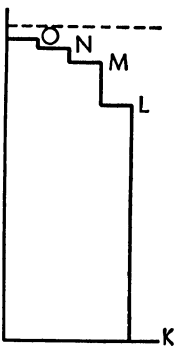


Fig. 19-14. Energy Levels in Hydrogen

Quantum Theory · We have good reasons for believing that energy, like matter, is not continuous but is made up of pieces. This is the quantum theory of energy structure. The energy carried by a ray of light travels in little bunches, or quanta. The magnitude of the energy in a quantum is directly proportional to the frequency of the light, or, in mathematical symbols,

$$E = h\nu,$$

where E is the energy of a quantum, h is a proportionality constant (known as the Planck constant), and ν is the frequency, or the number of waves passing a point in a unit of time. Since wave length is inversely proportional to frequency, it follows that the quanta of long waves, like radio waves, carry very little energy, and that the quanta get larger and larger as we proceed to shorter and shorter waves, through the whole known spectrum of frequencies, through heat waves, and infrared, the visible, the ultraviolet, to X rays, gamma rays, and finally to the gammas of the cosmic rays, which have the shortest wave length, the greatest frequency, and the largest quanta.

For example, in the hydrogen atom (Fig. 19-13) the electron in the *K* level, when it is exposed to an inflow of energy, is not lifted out of its position at all,

unless and until the quantum of energy which it receives is big enough to lift it all the way to, say, the *L*, or to the *M* or higher level. The energy transfers which occur between light rays, electrons, atoms, and molecules are in quanta, a discontinuous, particle-of-energy exchange. When we are working with large quantities of energy involving a huge number of quanta, the small-piece structure of the energy is apparently obliterated, or smoothed out.

Atoms of atomic number greater than 1 also contain a number of electrons equal to their atomic number, and, in the Bohr theory, each of these electrons circulates in a shell, or energy level. The question then is, how many electrons are there in each shell? Evidence from the periodic table, immediately following, shows that the *K* shell will hold no more than 2 electrons, the *L* shell will hold as many as 8, and the *M* shell 18.

2. EVIDENCE FROM PERIODIC RELATIONSHIPS

Periodic Arrangement of Electrons · From the periodic table of the previous chapter let us take the first 20 elements (Fig. 19-15). The elements in the vertical columns are similar. The periodic recurrence of properties noted in this arrangement of elements cannot be due to the

H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	A
K	Ca						

Fig. 19-15. First Twenty Elements

nuclear charge (atomic number), which increases regularly as we go from the lightest to the heaviest atom. Therefore it must be a function of some periodicity in the arrangement of the electrons of the atoms of the elements.

The hydrogen atom has a nuclear charge of 1, and 1 electron. The helium atom has a nuclear charge of 2, and 2 electrons. The helium atom is stable and unreactive, indicating that this arrangement of 2 electrons in the *K* shell is a very stable one. An atom of lithium, which possesses 3 electrons, very readily loses one of them to form a lithium ion (Li^+). To explain this we must assume that this behavior of the third electron represents an entirely different type of electron arrangement. So we suppose that this electron is placed in the next outer shell, the *L* shell, where it is not held nearly so tightly by the nucleus as the

other 2 electrons, deeper down in the K shell. Confirmatory evidence for this reasoning lies in the fact that the atomic volume of lithium is much greater than that of helium.

Beryllium, the next atom in the series, has a total of 4 electrons, 2 of which are very easily removed to form the beryllium ion (Be^{++}); and correspondingly, these 2 electrons are in the L shell. Similarly, as we continue up the series, increasing the nuclear charge a step at a time, the atoms B, C, N, O, F, will have respectively 3, 4, 5, 6, 7 electrons in orbits in the L shell. Finally we come to neon, which has 8 L electrons. It happens that an outer shell of 8 electrons is very stable, and shows very little tendency to part with any of its electrons or to take on any new electrons in its shell (L shell). Neon thus resembles helium in its stability, and in fact in many of its other properties.

When we come to the element sodium, with 11 electrons (two of which are K-shell electrons, close to the nucleus), we again observe a great readiness to lose 1 electron, associated with a greatly increased atomic volume. Consequently, to indicate this difference from the behavior of the other 10 electrons, we represent the sodium atom with 1 outer electron in the M shell. Proceeding through the series of atoms in the second row, we fill up the M shell step by step, until we come to argon (Fig. 19-15), where again the outer shell contains 8 electrons and is very stable. Potassium, the next atom, will have a single electron in the N shell, and will of course resemble sodium and lithium, not only in the ease with which it ionizes (K^+) but also in its spectroscopic and other types of behavior.

From these few illustrations the student will readily grasp the idea that from a consideration of the periodic relationships of the elements we can set up a theory of the arrangement of the electrons to account for the periodic recurrence of resemblances among the atoms.

3. EVIDENCE FROM IONIZATION POTENTIALS

The ionization potential of an element is the energy necessary to remove an electron from an atom in the gaseous state to form a positive ion. The energy then required to remove a second electron is known as the second ionization potential. Similarly we speak of the third, fourth, etc., ionization potentials, as electrons are removed in steps from the more and more highly charged ions. The ionization potentials can be determined experimentally. The results of such experiments for the elements in the first rows of the periodic table are shown in the table on page 332.

IONIZATION POTENTIALS*								
ELEMENT	FIRST	SECOND	THIRD	FOURTH	FIFTH	SIXTH	SEVENTH	EIGHTH
H	13.6							
He	24.6	54.4						
Li	5.4	75.6	122.4					
Be	9.3	18.2	153.9	217.7				
B	8.3	25.1	37.9	259.3	340.1			
C	11.3	24.4	47.9	64.5	392.0	489.8		
N	14.5	29.6	47.4	77.5	97.9	551.9	666.8	
O	13.6	35.1	54.9	77.4	113.9	138.1	739.1	871.1
F	17.4	35.0	62.6	87.2	114.2	157.1	185.1	953.6
Ne	21.6	41.1	64	97.2	126.4	157.9	—	—
Na	5.1	47.3	71.7	98.9	138.6	172.4	208.4	264.2
Mg	7.6	15.0	80.1	109.3	141.2	186.9	225.3	266.0
Al	6.0	18.8	28.4	120.0	153.8	190.4	241.9	285.1
Si	8.1	16.3	33.5	45.1	166.7	205.1	246.4	303.9
P	11.0	20.0	30.2	51.4	65.0	220.4	263.3	309.3
S	10.4	23.4	35.0	47.3	72.5	88.0	281.0	328.8
Cl	13.0	23.8	39.9	53.5	67.8	96.7	114.3	348.3
A	15.8	27.6	40.9	59.8	75.0	91.3	124.0	143.5
K	4.3	31.8	46	60.9	—	99.7	118	155
Ca	6.1	11.9	51.2	67	84.4	—	128	147

*The values are given in electron-volts. One electron volt is the energy required to move an electron through a potential difference of one volt; it is equivalent to 1.6×10^{-19} joules.

Notice that the energy required to remove the first electron from the elements in a row across the periodic table, for example, from Li to Ne, increases with increasing atomic number, being greatest at Ne (and He and A). This is to be expected from the increase in nuclear charge. Further increase in atomic number, however, from Ne to Na (or He to Li, A to K) shows an abrupt drop in ionization potential. It is thus unexpectedly easy to remove an electron from sodium, lithium, or potassium. It is very difficult, however, to remove a second electron from these atoms. These facts suggest that one of the electrons in these atoms is not very firmly held. Similarly, two electrons are easily removed from beryllium, magnesium, and calcium, but the third only with difficulty. The staircase line across the table represents the separation between easy removal and difficult removal. We deduce then that Be, B, C, etc. have 2, 3, 4, etc. electrons in an easily removed outer shell, and the rest in more stable inner shells. Thus, one may gain an insight into the probable arrangement of at least some electrons in the different atoms.

4. SUBSHELLS IN THE ATOM

From what has gone before, it is now evident that an alkali metal such as sodium has 1 electron in the outer shell, loosely held. If we regard the nucleus and the two inner electron shells of sodium as a core or kernel, then the atom has a similarity to the hydrogen atom, with a single electron revolving about a positively charged kernel. We might expect such a configuration to give a spectrum similar to that of hydrogen, as the electron jumps between the orbits external to the kernel. This is, in fact, the case, but instead of 1 set of converging spectral lines like those shown in Fig. 19-13, 4 such sets are observed, known as the sharp, principal, diffuse, and fundamental series. The explanation that there are within each energy level certain sublevels, or subshells, so that electron transitions from a subshell of one shell to another subshell in a different shell give rise to the spectral lines observed. These subshells are labeled according to the initial letters of the series named above, *s*, *p*, *d*, *f*.

Agreement with experiment is obtained if the first shell has only an *s* subshell, for its 2 electrons. The second shell has an *s* subshell capable of holding 2 electrons and a *p* subshell with space for 6, making a total space for 8 electrons in the second shell. The third shell has an *s*, a *p*, and a *d* subshell, capable of holding 2, 6, and 10 electrons, respectively, for a total of 18. The fourth has an *s* (2), a *p* (6), a *d* (10), and an *f* (14) subshell, total 32.

Study of the energy relationships further shows that the energy of an electron in a *d* or *f* subshell is greater than that of an electron in the *s* or *p* subshell of the next higher main shell, so that, if the main shells are numbered, the order of increasing energy is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s\ (< 4f < 5d) < 6p < 7s\ (< 5f < 6d)$$

Long Periods and Atomic Structure · On page 330 and in Fig. 37-2 the filling of the energy levels, or shells, as the nuclear charge increases stepwise for the first 20 elements is indicated. The electrons go into levels of higher and higher energy as the lower levels are filled; 20 electrons will fill the 1 *s*, 2 *s*, 2 *p*, 3 *s*, 3 *p*, 4 *s* subshells. The 21st electron in the element scandium, atomic number 21, will not go into the outer, or valence shell, but according to the scheme above, will enter the inner, 3 *d*, subshell. This then fills with its quota of 10 electrons as the atomic number increases from 21 to 29, before additional electrons go into the outer shell. This gives a series of 10 elements with only 2 electrons in the outer shell, as shown in the table on page 334. Elements of this sort, in which an inner subshell is partly filled, are known as *transition elements*.

ELECTRON CONFIGURATIONS SHOWING FIRST TRANSITION SERIES

AT NO	ELEMENT	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s
18	A	2	2	6	2	6						
19	K	2	2	6	2	6		1				
20	Ca	2	2	6	2	6		2				
21	Sc	2	2	6	2	6	1	2				
22	Ti	2	2	6	2	6	2	2				
23	Va	2	2	6	2	6	3	2				
24	Cr	2	2	6	2	6	5	1				
25	Mn	2	2	6	2	6	5	2				
26	Fe	2	2	6	2	6	6	2				
27	Co	2	2	6	2	6	7	2				
28	Ni	2	2	6	2	6	8	2				
29	Cu	2	2	6	2	6	10	1				
30	Zn	2	2	6	2	6	10	2				
31	Ga	2	2	6	2	6	10	2	1			
32	Ge	2	2	6	2	6	10	2	2			
33	As	2	2	6	2	6	10	2	3			
34	Se	2	2	6	2	6	10	2	4			
35	Br	2	2	6	2	6	10	2	5			
36	Kr	2	2	6	2	6	10	2	6			
37	Rb	2	2	6	2	6	10	2	6			1

A similar series of transition elements occurs from yttrium to silver (39 to 47) where the 4 *d* subshell is being filled, and lutetium to gold (71 79) where the 5 *d* subshell is being filled. The elements 57–71 are a special type of transition element known as the lanthanide series, in which the 4 *f* shell is being filled to its maximum of 14. As shown by the energy relations on page 333 this occurs only after the 5 *s*, 5 *p*, and 6 *s* shells have been filled, and gives these elements a special set of properties (Chap. 37). A similar situation exists for the elements starting with actinium, element 89, where the inner 5 *f* shell is filling.

The table above and the table of electron configurations in the Appendix show that no element in the free state ever has more than 8 electrons in its outer or valence shell, pointing again to the great stability of that configuration.

5. EVIDENCE FROM CHEMICAL COMBINATION

We have shown (Chap. 4) that the formation of chemical compounds, both electrovalent and covalent, the phenomena of electrovalence and covalence, and the formulas of compounds may be explained by and are consistent with the theory of atomic structure we have been presenting. A further discussion of these matters is given in the next chapter. Since the ultimate test of any theory is its ability to explain the facts, the usefulness of our theory is apparent.

QUESTIONS

1. Define (*a*) *electron;* (*b*) *proton;* (*c*) *neutron;* (*d*) *alpha particle;* (*e*) *atomic number;* (*f*) *isotopes;* (*g*) *spectrum;* (*h*) *transition elements;* (*i*) *ionization potential;* (*j*) *electrovalent compound;* (*k*) *covalent compound;* (*l*) *valence electrons;* (*m*) *nucleus;* (*n*) *inert-gas configuration;* (*o*) *radioactivity;* (*p*) *beta particle;* (*q*) *gamma ray.*

2. Give experimental evidence which indicates that (*a*) the nucleus is made up of several components; (*b*) the atom is porous; (*c*) the nucleus is positively charged and has a small volume compared with the size of the atom as a whole; (*d*) the electrons are located in shells around the nucleus; (*e*) many elements have isotopes; (*f*) the electron affinities of the atoms differ from one another.

3. Explain how it is possible for the nucleus of an atom to be many thousands of times more dense than the atom itself.

4. What is the composition of the nucleus of each of the following atoms: (*a*) titanium, at. no. 22, mass number (mass no.) 48; (*b*) arsenic, at. no. 33, mass no. 75; (*c*) indium, at. no. 49, mass no. 115; (*d*) cesium, at. no. 55, mass no. 133?

5. What is the composition of the nuclei of the isotopes of (*a*) potassium (at. no. 19) having the mass numbers 39 and 41, and those of (*b*) strontium (at. no. 38) having the mass numbers 86, 87, and 88?

6. Draw a diagram showing the arrangement of electrons (*a*) for the atoms of calcium and oxygen; (*b*) for the ions of calcium and oxygen; (*c*) for the compound calcium oxide.

7. When an atom of thorium (at. no. 90, mass no. 232) disintegrates by loss of an alpha particle, what element remains? What is its atomic number? its mass number?

8. When an atom of radioactive lead (at. no. 82, mass no. 214) disintegrates by loss of a beta particle, what element is left? What is its atomic number? its mass number?

9. For each of the following particles give the sign of the charge, the magnitude of the charge, and the mass: (*a*) proton; (*b*) electron; (*c*) lithium atom; (*d*) chloride ion; (*e*) magnesium ion; (*f*) alpha particle; (*g*) hydrogen ion; (*h*) sulfide ion; (*i*) magnesium nucleus; (*j*) potassium nucleus.

10. Draw a diagram showing the atomic structure of (*a*) a sodium atom; (*b*) a fluorine atom; (*c*) a magnesium atom.

11. (*a*) How does the theory of atomic structure explain the production of lines of characteristic colors in the spectra of the elements? (*b*) Why are there so many lines in the hydrogen spectrum, though the hydrogen atom contains only one electron?

12. The densities of the elements As (33), Se (34), Br (35), Kr (36), and Rb (37), as solids or liquids, are approximately 5.7, 4.8, 3.1, 2.6, and 0.86. How do you account for the rather abrupt change between krypton and rubidium?

CHAPTER 20

PHYSICAL AND CHEMICAL PROPERTIES OF ELEMENTS AND COMPOUNDS IN THE LIGHT OF THEIR ATOMIC STRUCTURE

The Driving Force in Chemical Reactions · While all that we have said, in the previous chapter, about the structure of atoms, is interesting and important, we have as yet said very little about the question which is of primary concern to chemists: Why do atoms combine (or react) with each other?

Atoms are held together, of course, by electrical forces. We know that the inert-gas atoms are extremely inert chemically and form no stable compounds. We know also that their outer shells hold 8 electrons (2 in the case of helium), and we feel sure that their chemical inertness is connected with the existence of a stable electron configuration. *All other atoms tend strongly to reach a stable electron configuration, usually that of the nearest inert-gas atom, by transfer of electrons from one atom to another, or by sharing electrons between atoms, and it is this tendency which results in the chemical combinations or chemical reactions of atoms.*

These two distinct ways, transfer or sharing, in which the electrons of the outer shells of two or more atoms may be redistributed during chemical action to give a stable configuration, result in the formation of two distinct types of compounds. These are called (1) electrovalent compounds, and (2) covalent compounds (see Chapter 4).

1. **Electrovalent compounds.** When a sodium atom, with 1 valence electron, meets a fluorine atom, which has 7, electron transfer occurs as represented in Fig. 20-1. This makes a complete octet around the fluorine because of the added electron; while the sodium also acquires the inert-gas structure, since its L shell now becomes the outer one. After giving up its electron, the originally neutral sodium atom is, of course,

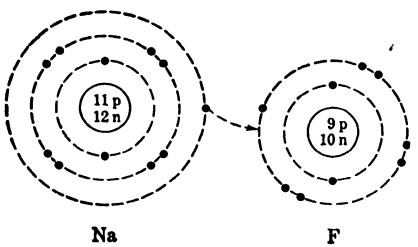


Fig. 20-1. The Combination of Sodium and Fluorine to Form Sodium Fluoride

positively charged; and the fluorine atom, accepting the electron, acquires a negative charge. In chemical symbols we may represent the transfer thus: $Na + F \longrightarrow Na^+ + F^-$. The two species of charged atoms (ions) are then attracted by electrostatic forces. Electrovalent compounds and, in general, most inorganic compounds are simply clusters of oppositely charged ions, formed by the surrender and gain of one or more electrons between atoms, and held together in definite ratios by electrostatic forces.

Examples. Sodium will also lose its electron to chlorine: $Na + Cl \longrightarrow Na^+ + Cl^-$; as will also potassium, which reverts to the argon shell: $K + Cl \longrightarrow K^+ + Cl^-$. Lithium, which envies the symmetry of its close neighbor helium, will also lend its electron to chlorine or fluorine: $Li + Cl \longrightarrow Li^+ + Cl^-$. When sodium reacts chemically with oxygen to form Na_2O, two atoms, each giving one electron, are necessary, since an oxygen atom needs two electrons to fill out its octet: $2\,Na + O \longrightarrow 2\,Na^+ + O^{--}$. But when Mg and Ca react with O to form MgO and CaO, a single atom of Mg and Ca will suffice, since each one carries two outer electrons: $Mg + O \longrightarrow Mg^{++} + O^{--}$; and $Ca + O \longrightarrow Ca^{++} + O^{--}$. Aluminum will react with chlorine to form $AlCl_3$, as follows: $Al + 3\,Cl \longrightarrow Al^{+++} + 3\,Cl^-$; and with oxygen, $2\,Al + 3\,O \longrightarrow 2\,Al^{+++} + 3\,O^{--}$, to give the compound Al_2O_3.

2. **Covalent compounds.** In many cases, especially among organic compounds, and in the make-up of complex ions such as SO_4^{--}, the constituent atoms cannot reach the desired condition of 8 outer electrons by a process of give and take, because both atoms have a deficit. So they resort to a different plan. Each atom contributes an electron to form a pair, held in common by both atoms, and considered a part of the outer shell of each. This pair of shared electrons constitutes a single bond and is called a covalent bond. Fig. 20-2 illustrates such a union between two fluorine atoms to make a fluorine molecule. Each atom had 7 outer electrons; by sharing a pair, each can claim 8. *Atoms held together by one or more pairs of shared electrons constitute covalent molecules.* The constituent atoms are closely bound into molecules, they are not oppositely charged, and they do not yield ions.

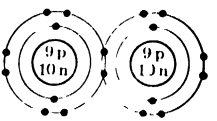


Fig. 20-2. The Fluorine Molecule (F_2)

Nitrogen will react with hydrogen to form ammonia (NH_3). Each hydrogen atom needs one more electron to make it similar to its neighboring inactive gas, helium; for the latter has but 2 electrons in its outer shell (Fig. 4-5). The nitrogen atom, with 5 electrons, needs 3 more to complete its number to 8. By sharing pairs of elec-

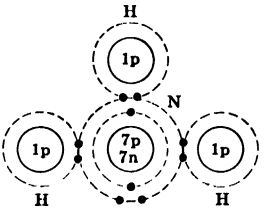


Fig. 20-3. Diagram of Ammonia

trons all four atoms acquire the inert-gas structure. The relations are indicated in Fig. 20-3.

Carbon will react with chlorine to form a compound called carbon tetrachloride (CCl_4). Fig. 20-4 is a diagram that indicates the distribution of the electrons in this compound. It will be remembered that carbon has but 4 electrons in its outer shell, and that it needs 4 more for completion, while each chlorine atom has 7 and needs but 1 more. Each chlorine atom shares 1 of its electrons with 1 of those of carbon, and this process provides 4 pairs of shared electrons, constituting 4 covalent bonds.

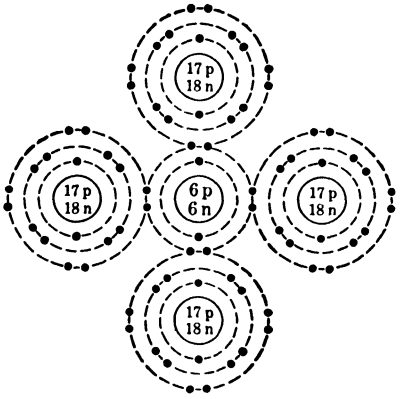


Fig. 20-4. Diagram of Carbon Tetrachloride

Representation of Covalent Linking · It is inconvenient to draw diagrams such as those in Fig. 20-4 to show covalent linking. So it is customary to represent a pair of electrons in the valence shell by a pair of dots. The fluorine atom is $:\ddot{\underset{\cdot\cdot}{F}}\cdot$; the fluorine molecule, $:\ddot{\underset{\cdot\cdot}{F}}:\ddot{\underset{\cdot\cdot}{F}}:$; and $H:\ddot{\underset{\cdot\cdot}{Cl}}:$ represents the hydrogen chloride molecule.

Electronic Theory of Valence · If we are right in assuming that chemical combination is due to the transfer of electrons from one atom to another, or to the sharing of pairs of electrons by atoms, then *the number of electrons transferred is the electrovalence of an element, and the number of pairs of electrons shared is the covalence.* An atom that takes up or loses 1 electron or shares a pair with another atom is a *univalent* atom. If it takes up or loses 2 electrons or shares 2 pairs, it is *bivalent.* In carbon dioxide (Fig. 20-5) the carbon atom shares 4 pairs of electrons with 2 oxygen atoms. The carbon atom is therefore *tetravalent*, each oxygen atom is bivalent, and the compound is covalent.

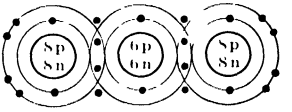


Fig. 20-5. Diagram of Carbon Dioxide

Valence Electrons · It will be observed that only the electrons in the outer electron shell are concerned in chemical actions and in determining the valence of an atom. The pair of K electrons, and those in inner completed shells, take no part in the action. Electrons in the outer incomplete shell are called *valence electrons.*

Positive and Negative Electrovalences · In electrovalent compounds it is often desirable to specify whether the electrovalence of an atom is due to the loss or to the gain of an electron. An atom that takes up one

or more electrons, and so becomes electrically negative, is said to have *negative* electrovalence; while an atom that loses one or more electrons, and thereby becomes electrically positive, is said to have *positive* electrovalence. Thus in sodium fluoride (Fig. 20-1) the sodium has a positive electrovalence of 1 and the fluorine has a negative electrovalence of 1.

Electrovalence of Complex Ions · Groups of atoms may form complex ions which have definite electrovalences. Sometimes, as in the case of the ammonium ion (NH_4^+), they have positive electrovalence. More often they are negative, as is the case with the nitrate ion (NO_3^-) and the sulfate ion (SO_4^{--}). The atoms within the ion are held together by covalent bonds.

Variations in Bond Types · While it is convenient and useful to classify compounds as electrovalent and covalent, this classification is somewhat oversimplified. Some covalent compounds react to leave ionic segments under certain circumstances, and many covalent compounds seem to have a partially ionic or polar character. With the background of the periodic table, atomic structure, and the way in which atoms combine, we have a logical basis for explaining the various types of chemical bonds in the light of the structures of atoms. Also, we may extend this explanation far enough to enable us to predict periodic behavior among the elements.

Relative Electron Affinity and Bond Type · Consider two atoms, M and N, each with at least one valence electron. Three different conditions may exist.

1. **M and N may differ greatly in their attraction for electrons.** In this case one will take an electron from the other:

$$M\cdot + \cdot N \longrightarrow M^+ + :N^-$$

As has been shown previously, the result is an electrovalent compound, made up of ions. We call the element with the larger attraction for electrons an electronegative element; the element with smaller attraction, electropositive. The bond formed is an electrovalent bond. The reaction between a sodium atom and a fluorine atom (p. 336) is a good example of this type.

2. **M and N may have about the same attraction for electrons.** In this case, as has been previously shown, neither can completely remove an electron from the other. Rather, they share a pair of electrons.

$$M\cdot + \cdot N \longrightarrow M:N$$

The resultant bond is called a covalent bond, and the compound is a covalent compound. It exists in the form of unit particles which we

have called molecules. The reaction between two fluorine atoms, or between nitrogen atoms and hydrogen atoms (p. 337), is a good example of this type.

3. **M and N may differ slightly in their electron-attractive powers,** not enough to permit complete electron transfer:

$$\mathrm{M}\cdot + \cdot\dot{\mathrm{N}} \longrightarrow \overset{\delta^+}{\mathrm{M}} : \overset{\delta^-}{\mathrm{N}}$$

In this case a true molecule is formed, but the molecule contains, in itself, differences in electric charge (called polarity) because of the displacement of the pair of electrons toward one of the atoms, indicated by the δ^+ and δ^- signs. Such a molecule, if placed between two electrodes of opposite charge, will tend to orient itself so that the positive end is near the negative electrode, and vice versa. Such a compound, while covalent, is said to be a *polar* compound, and the bond is called a polar-covalent bond. Hydrogen chloride is a good example of this kind of compound.

Thus we see that bond-type is largely determined by the relative attraction of atoms for electrons. The question naturally arises, why do atoms of different elements differ in their attraction for electrons? We may gain some insight into this problem by considering the structure of atoms.

Factors Affecting Electron-Attractive Power · From the point of view of atomic structure one may conclude that there are three factors affecting the electron affinity of atoms. These are (1) the charge on the nucleus of an atom, (2) the distance of the electrons from the nucleus, and (3) the shells of electrons which intervene between the electron in question and the nucleus.

1. **Effect of the charge on the nucleus.** Other things being equal, it is apparent that the attraction of an atom for an electron is a function of the nuclear charge. The greater the charge, the greater the force with which the electron is attracted to the atom.

2. **Distance of the electron from the nucleus.** Again other things being equal, it is entirely logical to believe that the attraction of the nucleus for an electron falls off rapidly with increasing distance of the electron from the nucleus. Since we are primarily concerned with valence electrons, this means that the size of the atom (determined by the outermost electrons) is an important factor in determining electron affinity.

3. **Intervening shells of electrons.** We have seen in studying the structure of atoms that, as the atomic number increases, the numbers of

electrons and their shells increase, to that in the case of atoms of high atomic numbers the valence electrons have, between them and the nucleus, large numbers of other electrons. Since all these are negatively charged, they repel the outer electrons; this weakens the force with which the outermost electrons are held.

These three factors are obviously interrelated. For example, the volume occupied by the atom will depend to some extent on the nuclear charge and on the number of intervening shells, and the latter, in turn, is a function of the nuclear charge. Nevertheless, it is possible to predict the properties of the elements and their compounds by use of these three concepts. Some examples are given below.

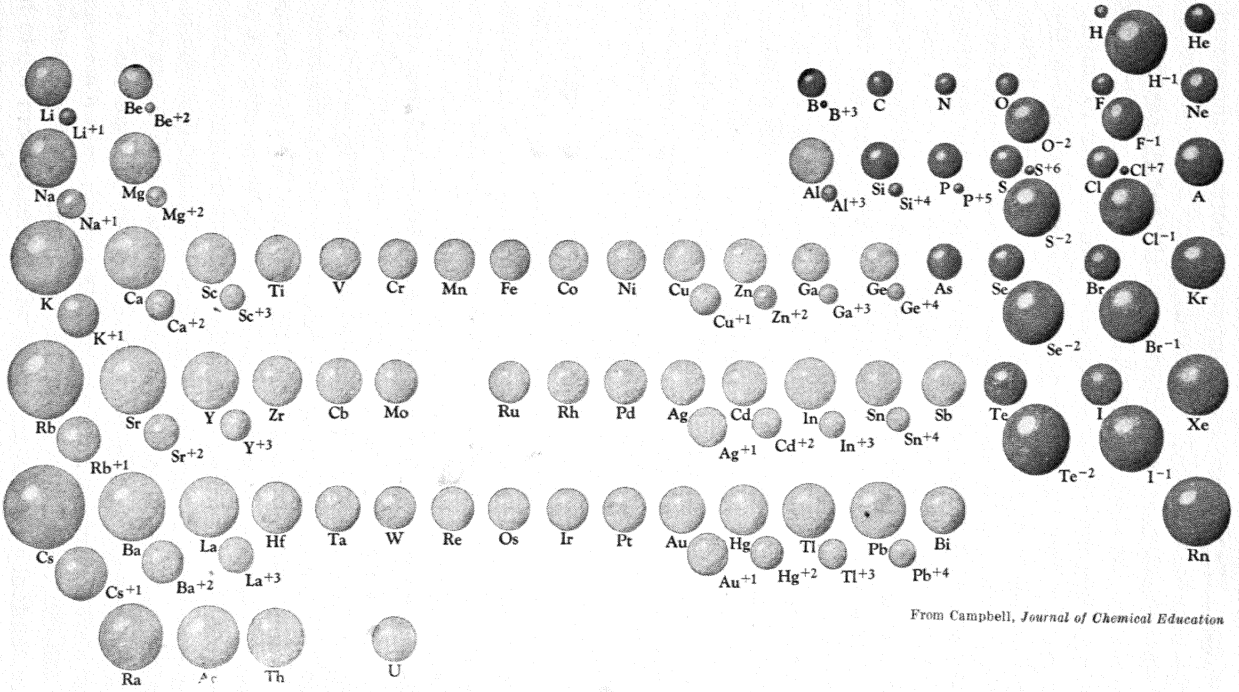
Predictions Based upon the Factors That Affect Relative Electron Affinity · **1. The tendency to lose electrons will decrease from left to right in the periodic table.** As the atomic number increases across the periodic table, the attraction of the nucleus increases. Since, in each of the first two periods at least, there is no increase in the number of shells, the first factor, the attraction of the nucleus, is the determining one. In consequence, the elements at the start of the series (excluding the rare gases, which are put in Group 0) are strongly electropositive and form positively charged ions, while elements such as fluorine have little or no tendency to give up electrons to other atoms.

For the same reasons, the atoms of elements at the right of the table are strongly electronegative. They tend to form ions by acquiring electrons. This tendency disappears with the formation of a complete octet, since the addition of more electrons would have to take place in an outer shell, where the attractive force is too small.

2. **Atomic size will, in general, decrease with increasing atomic number across the table.** As long as no new intervening shells are formed, the attraction of the nucleus for a valence electron will increase, and the valence shell will grow smaller as the charge on the nucleus increases. Compare the atomic sizes of Na, Mg, Al, Si, P, S, and Cl in the second row of Fig. 20-6. (There is a secondary increase in size observable in the transition elements when the inner shells have filled up.)

It is noticeable also that the size of the ion is small as compared with the size of the atom among the electropositive elements (which lose electrons to form ions); but the size of the ion is larger than the size of the atom in the electronegative elements (which gain electrons to form ions). Compare Na with Na^+, and Br with Br^-, in Fig. 20-6.

3. **The tendency to lose electrons will increase from top to bottom of the table in a given group.** Since, according to our theory of atomic structure, the difference between the elements in a family lies in the number of



From Campbell, *Journal of Chemical Education*

Fig. 20-6. Periodic Table Showing Relative Sizes of Atoms and Ions · Scale: 0.2 cm = 1 angstrom unit

electron shells (and, in consequence, in the size of the atoms), the valence electrons of the elements of higher atomic numbers will be farther removed from the nucleus and will be shielded by a greater number of inner shells of electrons. These two effects more than offset the greater nuclear charge. We may confidently predict, for example, that rubidium will have a greater tendency to ionize than potassium, and that the ionizing power of cesium will be still greater. We can, in the same way, predict that electrons can be removed from the iodide ion to form the free element more readily than from the bromide ion.

Experimental Testing of These Predictions; Ionization Potential. We may now review the ionization potentials (p. 332) of the elements in the light of atomic structure and periodic behavior. Below are presented some tables showing the experimental results for the elements arranged by periods and by families.

IONIZATION POTENTIALS (VOLTS) OF THE ELEMENTS BY PERIODS

PERIOD I							
H 13.6							He 24.6
PERIOD II							
Li 5.4	Be 9.3	B 8.3	C 11.3	N 14.5	O 13.6	F 17.4	Ne 21.6

IONIZATION POTENTIALS OF THE ELEMENTS BY FAMILIES

GROUPS I A, II A, VI B, and VII B

Group I A		Group II A		Group VI B		Group VII B	
Li	5.4	Be	9.3	O	13.6	F	17.3
Na	5.1	Mg	7.6	S	10.4	Cl	13.0
K	4.3	Ca	6.1	Se	9.8	Br	11.8
Rb	4.2	Sr	5.7	Te	9.0	I	10.4
Cs	3.9	Ba	5.2				

You will notice that the energy required to remove an electron increases from left to right in the periodic table, and decreases from top to bottom in a family.

Metals and nonmetals. Those elements which easily lose electrons to form positive ions are called metals. In the free state, metals will conduct the electric current readily. This is easily explained in terms of loosely held valence electrons, which move readily from one place to another within the metal, transporting the electric current.

Elements which hold electrons firmly and tend to gain electrons to form negative ions are called nonmetals. In the free state they will not conduct the electric current.

Acid and base properties. The metals form hydroxides which act as bases. Thus, sodium hydroxide (NaOH) is a base because the electrons are more firmly bound to the electronegative element oxygen than to the sodium. In consequence this compound ionizes to give Na^+ and $\left(:\ddot{O}:H\right)^-$ ions.

The hydroxide of chlorine (hypochlorous acid, HOCl) on the other hand, is acidic. The electronic formula of this compound, if it were completely symmetrical would be:

$$:\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{O}}:H$$

Chlorine is a strongly electronegative element; therefore the electrons which form the covalent bond between oxygen and chlorine are pulled toward the chlorine. Oxygen, however, is also an electronegative element, and does not give up its electrons entirely to the chlorine. But the pull of the chlorine nucleus causes the electrons of the covalent bond between oxygen and hydrogen to be pulled closer to the oxygen. The result is a distortion in the electron density, which may be represented as follows:

$$:\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{O}}:H$$

The hydrogen, which is intermediate in the strength with which it holds electrons, thereby has its positive nature enhanced, and it is easily removed as a proton by a water molecule, with the formation of a hydronium ion.

Since, within a given family, the electron becomes more loosely held as the atomic number increases, the metallic properties tend to become more pronounced, and the ability to form basic hydroxides also increases, as the atomic number and the size of the atom increase.

The result is that metallic properties are most pronounced at the left and lower part of the periodic table (the extended form of the periodic table, p. 313, shows this better than the Mendeleev table). Conversely, the acid-forming properties of the hydroxides of the elements are more pronounced at the right and top of the table. In Fig. 20-6 this is indicated by using heavily shaded circles to represent nonmetals and lightly shaded circles to indicate metals. Elements on the border line may sometimes act as metals and sometimes as nonmetals. Thus, aluminum

hydroxide will act as a base in the presence of a strong acid and as an acid in the presence of a strong base.

Other Bond Types · In addition to the purely electrovalent, the purely covalent, and the polar-covalent bond types described earlier in the chapter, certain other bond types may be described.

1. **Multiple bonds.** A covalent bond is formed when two atoms share a pair of electrons. In some cases two atoms may share two pairs of electrons, forming a *double bond,* or three pairs, forming a *triple bond.* Such bonds are common in the compounds of carbon; the bonds in carbon dioxide and the poisonous gas hydrogen cyanide are examples:

$$\ddot{O} :: C :: \ddot{O} \qquad H : C ::: N :$$

Note that carbon, the oxygens, and nitrogen have eight electrons in the outer shell, and hydrogen two, corresponding to the inert gas configuration. Multiple bonds are in many cases fairly reactive, since they may be "opened" to form single bonds; thus water reacts with carbon dioxide as HOH,

$$\ddot{O} :: C :: \ddot{O} + H : \ddot{O} : H \longrightarrow \ddot{O} :: \underset{:\ddot{O}:}{\overset{H}{C}} : \ddot{O} : H$$

attaching a hydrogen to a carbon dioxide oxygen, and the OH to the carbon.

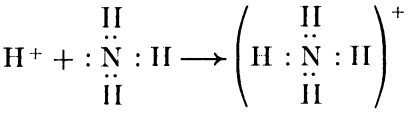
Multiple bonds of this sort are rarely formed by elements other than those in the first row of the periodic table, Be to O. The reason for this is not clear, but it may be that only small atoms are capable of forming multiple bonds.

2. **Co-ordinate bonds.** The common type of covalent bond is formed when atoms share a pair of electrons, one of which is provided by each atom. There is another type, however, called the co-ordinate bond (or the co-ordinate covalent bond) which is best pictured as being formed when one of the atoms provides both electrons. Several examples of co-ordinate bonds are given below. The co-ordinate bond, once formed, has properties like those of any other covalent bond.

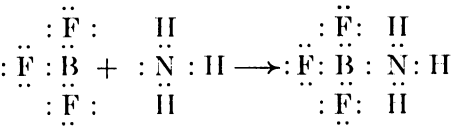
Case 1 · When water comes in contact with the covalent compound hydrogen chloride (HCl), a hydronium ion is formed (see page 239). This may be interpreted as resulting from the formation of a co-ordinate bond between a water molecule and a hydrogen ion (proton):

$$H^+ + : \underset{\ddot{H}}{\overset{\ddot{}}{\ddot{O}}} : H \longrightarrow \left(H : \underset{\ddot{H}}{\overset{\ddot{}}{\ddot{O}}} : H \right)^+$$

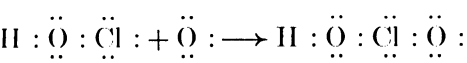
Case 2 · Ammonia reacts in much the same way with a hydrogen atom (proton):



Case 3 · Boron trifluoride (BF_3), in which the boron atom is 2 electrons short of a complete octet, readily adds to ammonia, which has an unshared pair of electrons:



Case 4 · The oxidation of hypochlorous acid to chlorous acid may be interpreted as resulting from the co-ordination of an oxygen atom which has 6 electrons, with a chlorine atom which has an unshared pair:



Complex Ions · Many simple ions, especially those of the transition elements, will form co-ordinate bonds with other ions or molecules to form complex ions ions containing more than one atom. Thus copper ion Cu^{++} will combine with four molecules of ammonia or water to form the complex ions $Cu(NH_3)_4^{++}$ and $Cu(H_2O)_4^{++}$. Other examples are

$Ag(NH_3)_2^+$	NH_4^+	$Al(H_2O)_6^{+++}$
$Cu(CN)_2^-$	SO_4^{--}	$Co(NO_2)_6^{---}$
	$Zn(OH)_4^{--}$	$Fe(CN)_6^{----}$

If the electronic structures of these are shown, it will be observed that only those in the middle column have 8 electrons in the valence shell of the central atom; the others, however, which have either less or more than 8, are also stable ions.

This is a very common situation in many complex ions. One reason for this variation in the number of electrons around the central atom in a complex ion is that some atoms or ions (such as those of the transition elements) can use an unfilled electron shell in the inner levels as "receivers" for electrons from other atoms or groups. In fact, some atoms can use an unfilled shell outside the valence shell to form complex ions; zinc and cadmium are examples of this kind of atom. Another reason is that the size of the central atom or ion determines how many other atoms or groups of atoms can arrange themselves around it, and

hence the number of electrons it will be sharing. These factors in complex formation will be discussed later (Chap. 37).

Lewis Acids and Bases · Co-ordinate covalent bonds are formed by reaction between an element, an ion, or a compound which has an unshared pair of electrons and one which has space for a pair of electrons. G. N. Lewis proposed that a particle that can accept a pair of electrons, such as BF_3 in Case 3, be called an acid, and that one which donates a pair of electrons, like NH_3, be called a base. The terms *Lewis acid* and *Lewis base* are often used to describe such compounds or ions.

The Hydrogen Bond · Covalent bonds between hydrogen and the small electronegative atoms fluorine, oxygen, and nitrogen are highly polar, with the hydrogen positive. When the hydrogen so bound comes close to another fluorine, oxygen, or nitrogen atom, the two are held together by electrostatic attraction. This attraction is so great that it has almost the effect of a definite bond in which the hydrogen forms a bridge between two electronegative atoms, and it has come to be called the hydrogen bond. This is shown for water in Fig. 20-8 in which the hydrogen bond is indicated by a dotted line.

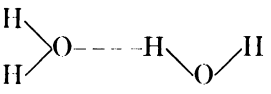


Fig. 20-8. Hydrogen Bond in Water

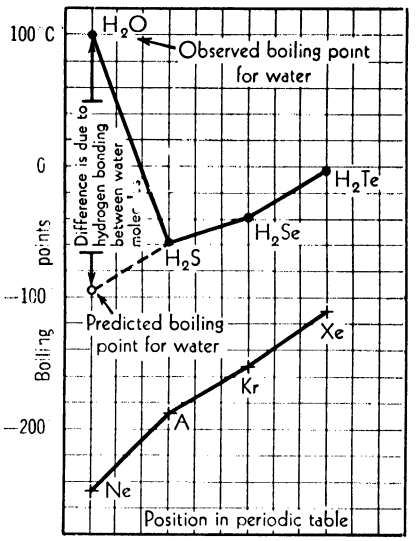


Fig. 20-7. Anomalous Boiling Point of Water · Showing, in the lower curve, the boiling points of four inert gases, decreasing with decreasing atomic number. In the upper curve there is a similar regular decrease in the case of the hydrides of tellurium, selenium, and sulfur. But the boiling point of water is much higher, almost 200° higher, than expected. The difference is attributed to hydrogen bonding between water molecules. (Redrawn from Taft and Sisler, "Hydrogen Bonding," *Journal of Chemical Education*, Vol. 24, p. 175, April, 1947; and from Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 1940, Fig. 39-1)

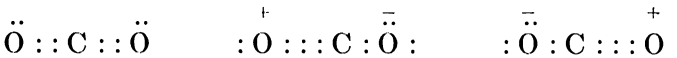
The effect of hydrogen bonding on the physical state of several molecules is readily apparent if the hydrogen compounds HF, H_2O, and NH_3 that form hydrogen bonds are compared with the corresponding compounds of neighboring elements in the periodic table, HCl, H_2S, PH_3, and CH_4, which do not form hydrogen bonds to any appreciable extent. The last four are gases at room temperature, indicating that the forces between molecules are not great enough to cause the molecules to stick together as a liquid. The

first three, however (HF, H_2O, and NH_3), are liquids or easily liquefied gases, pointing to the strong hydrogen bonds between molecules in these compounds. The effect of hydrogen bonding on the boiling point of water is shown in Fig. 20-7. In the case of hydrogen flouride, the hydrogen bond is so strong that the ion FHF^- has an independent existence in the salt K^+, FHF^-.

The Metallic Bond · Attention has already been called (pp. 343–344) to the difference between metals and nonmetals. Atoms of metallic elements have only a few electrons in the outer shell, and cannot combine with each other to form a stable inert-gas configuration. Rather, the nuclei and inner shells arrange themselves in an orderly array and let the valence electrons roam where they will through this array. From one point of view the valence electrons do not belong to any one atom or pair of atoms, but serve only as a sea of negative electricity to keep the positive atom kernels from repelling each other. From another point of view, the electrons form covalent bonds between pairs of atoms; but the bonds are continually shifting, so that now one pair, now another, are connected. This shifting again gives a freedom of movement to the electrons, making the metal a good conductor. Metals also are readily deformed, showing the properties of malleability and ductility rather than brittleness, because the shifting of bonds makes it easy for old bonds to break and new ones to form in the new positions of the atom kernels after deformation.

Resonance · In formulating the structure of many covalent or polar-covalent molecules we usually try to find a structure which shows a complete octet for each atom. Sometimes we find that several different structures satisfying this requirement may be written. If these structures are different only because the position of electrons has been changed, with no rearrangement in the positions of the atomic nuclei, then we find experimentally that the molecule is more stable than we would have predicted by looking at any one of the possible structures. We say that the molecule has been stabilized by *resonance* between the different forms, although we know that the actual structure does not correspond at any time to any one of the forms, but rather to a form which contains features of all of them.

Resonance structures are common among molecules which contain multiple bonds. Thus the electronic formula of carbon dioxide can be written in at least two other ways than that given on page 345:



Each formula shows the sixteen valence electrons arranged with eight

electrons for each atom, with no disturbance in the linear O—C—O arrangement of the nuclei. The positive and negative signs indicate that, allotting each atom one of the electrons in each shared pair, the left-hand oxygen in the center formula has only five electrons in its valence shell, one less than the six required for a neutral oxygen atom, while the right-hand oxygen has seven electrons in its valence shell, one more than the originally neutral atom. The actual structure of the carbon dioxide molecule does not correspond to any one of the three; the fact, however, that it is possible to write three structures, differing only in the position of electrons, tells us that carbon dioxide will be a more stable substance than would be expected by looking at the left-hand formula.

Bond Type and the Properties of Compounds

CRYSTAL FORM AND STRUCTURE

Electrovalent Compounds · Crystals of electrovalent compounds are clusters of ions held to each other by powerful electrostatic forces. The ions do not pair off, but rather arrange themselves in a crystal lattice in such a way that each positively charged ion is surrounded by negatively charged ions and is attracted to each of them. Similarly, the negatively charged ions are surrounded by positively charged ions and are attracted to them impartially. In consequence, the ions in the crystals are rigidly held in place. As a result, the melting point is high, and the crystals are very hard, but brittle. Electrovalent compounds are often soluble in water, because of the ease with which the polar-covalent water molecules attach themselves to the ions which are thus hydrated. The solutions will conduct an electric current. Common salt is a typical electrovalent compound.

Covalent Compounds · Crystals of covalent compounds, in contrast to electrovalent compounds, are clusters of molecules held to each other by weak van der Waals forces. The crystals are easily deformed, because it requires little force to push the molecules past each other. The melting point of these compounds is low, for the same reason, and the vapor pressure is high, because only a slight increase in temperature is enough to give the molecules sufficient energy to permit them to separate from each other. In fact, the forces between the molecules of covalent compounds are so weak that these compounds of low molecular weight are gases or liquids at room temperature, for example CH_4, CCl_4; those of high molecular weight are liquids or solids (see the table of hydrocarbons, Chap. 28). This is in accord with a general principle of chemistry,

that boiling points and melting points of similar compounds increase with increasing molecular weight.

Polar-Covalent Compounds · The molecules of polar-covalent compounds are attracted to each other more than the molecules of covalent compounds, because of the electrostatic attractions involving the positive and negative ends of the polar-covalent bonds in different molecules. Hence the boiling points and melting points will be higher for polar-covalent compounds than for covalent compounds of similar molecular weight; the polar-covalent compound may be a liquid, while the covalent compound is a gas, for example, H_2O and CH_4. This effect will be most marked in those compounds of highly polar character which show hydrogen bonding.

Large-Molecule Covalent Compounds · It has been mentioned above that, other things being equal, high molecular weight is associated with high boiling point. This is particularly true of molecules that have a threadlike or chainlike structure (such as cellulose), or molecules that have a three-dimensional structure like diamond (p. 484) or quartz (p. 497). There are several reasonable explanations for this, for example:

1. The van der Waals forces which hold molecules together will be greater as the surface of contact between molecules is greater. This is also true of forces due to hydrogen bonding, and other polar forces. Consider the two compounds *A* and *B*, *A* being made up of small and approximately round molecules, *B* of larger and more threadlike molecules (Fig. 20-9). The van der Waals forces holding molecules of *A* to each other will be much smaller than those holding the molecules of *B* to each other, because the molecules of *A* are smaller than those of *B*, and because the surface of contact is less.



Fig. 20-9

2. Chain molecules can become entangled with each other and held together as a result of this entanglement. A good analogy is to visualize two beakers, one full of BB shot, the other of short lengths of chain or pieces of string. The shot can be poured out of the beaker, like water, but the chain or string is more difficult to pour. It may be pointed out, incidentally, that solutions of chainlike molecules are viscous (like molasses), partly for this reason.

3. Giant molecules may form, with bonds in three dimensions, and large enough to see and handle. This is the case with diamond (p. 484),

which is made up of carbon atoms. An atom of carbon has four valence electrons, and forms four covalent bonds. If it forms covalent bonds with other carbon atoms, these can in turn combine with still other carbon atoms, building up a large crystal in which all atoms are connected by covalent bonds. This molecule is now so large that it can be vaporized only by breaking it into smaller fragments. To do so requires that the strong covalent bonds be broken; this requires the large energy available only at high temperatures.

Similar giant three-dimensional molecules are present in the hard, infusible plastics like Bakelite (Chap. 32), which do not melt or vaporize on heating until after they have decomposed into smaller fragments by the breaking of the covalent bonds.

QUESTIONS

1. Why do atoms combine with one another? Illustrate your answer.

2. In what three ways may atoms acquire an inert-gas configuration?

3. (*a*) What factors affect the relative electron affinities of atoms? (*b*) How do the relative electron affinities of the elements vary with (1) the increase in atomic number from sodium to argon; (2) the increase in the atomic weight in a family? (*c*) How can the difference in relative electron affinities be used to account for (1) the fact that some elements are metals and others are nonmetals; and (2) the fact that the hydroxides of some elements are acids and those of others are bases?

4. Hydrogen sulfide (H_2S) is a weaker acid than hydrogen selenide (H_2Se), but sulfuric acid (H_2SO_4) is a stronger acid than selenic acid (H_2SeO_4). Account for this in terms of atomic structure.

5. Draw a diagram showing the arrangement of the valence electrons for (*a*) chloroform ($CHCl_3$); (*b*) phosphorus trichloride (PCl_3); (*c*) the perchlorate ion (ClO_4^-); (*d*) the sulfate ion (SO_4^{--}); (*e*) bromic acid ($HBrO_3$); (*f*) the bromate ion (BrO_3^-).

6. What is a double bond? a triple bond? Draw an electronic structure for CO_2 (two double bonds); for N_2 (a triple bond).

7. Draw an electronic diagram showing all the valence electrons in the complex ion $Cu(NH_3)_4^{++}$.

8. How do you explain the fact that water is a liquid at ordinary temperatures, whereas one would expect it to be a gas? How would you explain the fact that HF has a higher boiling point than HCl?

9. Draw a diagram showing the valence electrons in $AlCl_3$. This compound is a Lewis acid. Why is it so called? How would you expect it to act with a Lewis base such as NH_3?

10. The nitrate ion, NO_3^-, has a "resonating" structure. Explain. Draw as many forms as you can of this ion, considering the three oxygen atoms as individuals.

CHAPTER 21

NUCLEAR REACTIONS; FISSION AND FUSION; RADIOTRACERS

Introduction · About two thousand years ago the alchemists set out on their quest of a method for transmuting the more common metals, especially the metal mercury, into gold; but they abandoned their attempt during the fifteenth century. Almost five hundred years later it was discovered that transformations of some of the elements into other elements have been taking place by a natural process, radioactivity, which we have already discussed in Chapter 19. Today it is not gold that we seek; the tremendous quantities of energy that result from such transmutations, as well as the radioactive light elements that can be produced (the "radiotracers"), are far more valuable to us than gold.

Nuclear Reactions and Artificial Radioactivity

We know that the nuclei of some of the heavy atoms are unstable, and that they spontaneously undergo radioactive disintegration, emitting alpha or beta particles. Even the nuclei of apparently stable atoms can be made unstable if they are bumped hard enough by certain bombarding particles; and such particles can be driven right into a nucleus. Then rearrangements among the protons and neutrons within the nucleus may occur (possibly resembling chemical reactions in some respects), a different nucleus may be produced, and certain product particles may be shot out. Such changes are called *nuclear reactions.* They have fascinated many physicists and chemists during recent years.

The course of nuclear reactions may often be followed by a study of the products formed by known reactants, just as with ordinary chemical reactions, and in nuclear reactions *individual particles* may often be studied to very great advantage.

Instruments for the Study of Particles · While we cannot see the flying pieces from the exploding atom, we have learned how to manipulate them in magnetic and electrostatic fields, and to direct them against photographic plates and fluorescent screens, and through various gases. Wherever they go they leave a trail of ions, and several ingenious instruments have been devised with which the particles may be detected and

counted and their kinetic energies measured, and other characteristics determined. From the results of such studies our present picture, or theory, of the inner structure of the atom has been developed.

The most important of these instruments are the electroscope, the spinthariscope, the Geiger counter, the cloud chamber, and the scintillation counter (which resembles the spinthariscope). The first three have already been described (see pages 321, 79, and 80).

The Cloud Chamber · In this instrument the particles under examination are allowed to travel in a gas space supersaturated with water vapor; and along their path they collide with gas molecules and ionize thousands of them. Water droplets condense on these ions, and thus render the track of the particle visible as a misty string of tiny water beads. The tracks may be photographed. From the character of the forks in these fog tracks, where nuclear disintegrations occur, the nature of the products of the disintegration can be inferred.

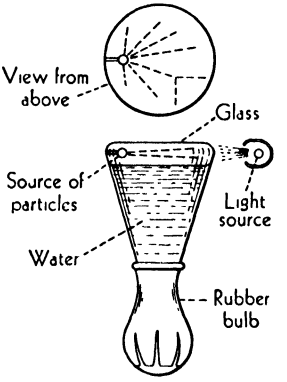


Fig. 21-1. Simplified Cloud Chamber The bulb is compressed to force water up into the chamber and is then suddenly released. The expanding air or other gas is thus chilled and becomes supersaturated with water vapor

Bombardment with Alpha Particles · As natural atom bullets for shooting a nucleus, the alpha particles are already available, since they themselves are shot as projectiles out of the nuclei of some radioactive atoms at terrific velocities (9000 to 14,000 miles per second, p. 320). In the first authentic case of a nuclear reaction (observed by Rutherford) an alpha particle entered the nucleus of a nitrogen atom, a proton was ejected, and an oxygen atom (isotope of mass 17) was left as the residue:

$$_{7}N^{14} + {}_{2}He^{4} \longrightarrow {}_{1}H^{1} + {}_{8}O^{17} \qquad (1)$$

The number above the symbol indicates the atomic mass (mass number) and the one below shows the atomic number (nuclear charge). Note that in a balanced nuclear equation, the sum of the mass numbers of the reactants must be equal to the sum of the mass numbers of the products; furthermore, the sum of the atomic numbers must be equal for reactants and products.

High-speed Particles · While other transmutations of this sort have been obtained by the reaction of alpha particles with the nuclei of the *light* elements, the much stronger repulsive force of the large positive charge on the nucleus of a *heavy* atom causes deflection of an alpha particle (Fig. 21-2) and prevents it from entering the nucleus. (Recall Rutherford's bombardment of gold foil with alpha particles, p. 324.) In order to drive an alpha particle into the nucleus of a heavy atom it

is desirable to be able to impart a very high velocity to the alpha particle, so high that the particle will be *driven into the nucleus in spite of the repulsive force.*

Other convenient bullets are the hydrogen ion (proton, ${}_1H^1$) and the heavy hydrogen ion (deuteron, ${}_1H^2$), which, however, are not natural bullets, and have to be accelerated from ordinary thermal velocities up to the very large velocities required to enable them to penetrate into nuclei. This is the reason for designing and building "atom-smashing" machines, such as the Van de Graaff electrostatic generator, the cyclotron, the linear accelerator, the synchrotron, and the betatron. These machines are used to accelerate bullet-particles to enormous velocities; the cyclotron, developed by Lawrence at the University of California, is the most common.

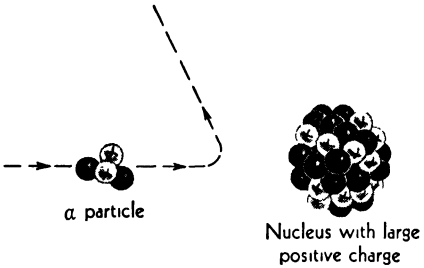


Fig. 21-2. Failure of an Alpha Particle to Penetrate into a Heavily Charged Nucleus

Cyclotron · The cyclotron (Fig. 21-3) consists of a massive electromagnet, between the two iron poles of which a flat, circular (brass) box fits, with the north pole of the magnet below and the south pole above (see front view). In the box

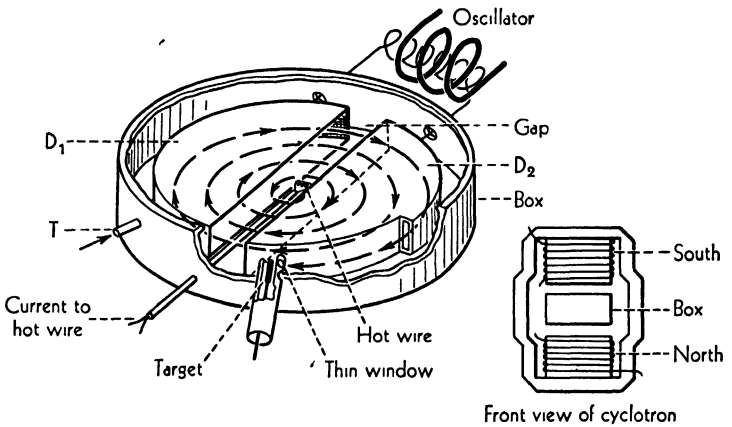


Fig. 21-3. Drawing Showing the Important Parts of the Cyclotron

are two "dees," or D-shaped sections, made by cutting a smaller, flat (brass) box, shaped like a pillbox, into halves. These two halves, D_1 and D_2, separated by a gap, are charged to a high potential difference (50,000 volts or more), one positively and the other negatively, by a high-frequency oscillator. A good vacuum is maintained in the box.

If protons are to be accelerated, a small quantity of ordinary hydrogen is admitted through the tube T, and is ionized by a hot wire. A proton (H^+) will first be repelled by D_2 (at first positively charged) and be attracted into section D_1 (negatively charged); and as it moves, it will follow a curved path in the magnetic field, as would be expected (pp. 144, 320). The timing is so arranged that when the particle again reaches the gap between D_1 and D_2, the charge on each "dee" is reversed, and the particle is repelled by D_1 and attracted by D_2. Reversal of the electric field is continued, and the particle gets a push each time it crosses the gap. It travels in an ever widening spiral until, at maximum speed, it is allowed either to issue from the cyclotron or to strike and penetrate the thin window of the tube containing the target and hit the target substance. After bombardment by many such bullet-particles the target substance can be removed for analysis or use.

Enormous magnets are required. The larger and stronger the magnetic field, the more frequently can the spiraling particle be made to cross the gap, and the greater its acceleration becomes. There are several cyclotrons in use with magnets weighing about 100 tons; and the speed acquired by protons may be 30,000 miles/sec or more. The present largest cyclotron, at the University of California, has a magnet that weighs about 2000 tons, with pole pieces 184 in. in diameter, and can accelerate a single deuteron to a kinetic energy of 200,000,000 electron-volts, or about 3.2×10^{-4} erg– equivalent to a speed of about 1.4×10^{10} cm/sec, or almost 87,000 miles/sec, almost half the velocity of light.

Bombardment with Protons and Deuterons · The stream of high-speed protons or deuterons, out of the cyclotron, may be directed at nuclear targets of various elements and a great variety of transmutations achieved. For example, lithium atoms of mass 6 and 7, when bombarded, respectively, with deuterons and protons, give helium atoms in both cases:

$$_3Li^6 + {}_1H^2 \longrightarrow 2\ {}_2He^4 \tag{2}$$

$$_3Li^7 + {}_1H^1 \longrightarrow 2\ {}_2He^4 \tag{3}$$

The heavier atom tellurium, when bombarded with deuterons, produces iodine and neutrons:

$$_{52}Te^{130} + {}_1H^2 \longrightarrow {}_{53}I^{130} + 2\ {}_0n^1 \tag{4}$$

Bombardment with Neutrons · In the bombardment of the nucleus the neutron is extremely effective because it carries no charge and is not repelled by the nucleus. When used for bombarding nuclei, neutrons must be knocked out of the nuclei of other atoms. There are several convenient methods for doing this. When the boron isotope of mass 11 is bombarded with alpha particles, neutrons (mass, 1; charge, 0) are produced:

$$_5B^{11} + {}_2He^4 \longrightarrow {}_0n^1 + {}_7N^{14} \tag{5}$$

Another excellent source of neutrons is provided by the bombardment of lithium (mass, 7) by deuterons direct from a cyclotron:

$$_3Li^7 + {}_1H^2 \longrightarrow {}_0n^1 + {}_4Be^8 \qquad (6)$$

An interesting and typical example of a neutron reaction is the following:

$$_{14}Si^{28} + {}_0n^1 \longrightarrow {}_1H^1 + {}_{13}Al^{28} \qquad (7)$$

The gain of a neutron and loss of a proton does not change the mass but reduces the atomic number from 14 to 13, and thus results in the transmutation of atoms of silicon into atoms of aluminum.

A reaction which is just the reverse of reaction (5) has been found to occur:

$$_7N^{11} + {}_0n^1 \longrightarrow {}_5B^{11} + {}_2He^4 \qquad (8)$$

So it seems that there may be reversible reactions in a nucleus. Some nuclear reactions are endothermic and others exothermic, and usually enormous quantities of energy (per gram-atomic weight transformed) are involved.

Artificial Radioactivity · In 1934 Professor Joliot and his accomplished wife (daughter of Madame Curie) discovered artificial radioactivity. They found, for example, that aluminum, when bombarded with alpha particles, is transmuted into radioactive phosphorus. The latter disintegrates in the manner of radioactive atoms, with a measurable half-life period (p. 322). In this way atoms of elements not normally radioactive may be made radioactive. In their decay these artificial radioactive elements usually emit either positrons or electrons (beta particles).

Aluminum bombarded with alpha particles yields radioactive phosphorus:

$$_{13}Al^{27} + {}_2He^4 \longrightarrow {}_{15}P^{30} + {}_0n^1 \qquad (9)$$

Then the phosphorus, with a half-life of 3 minutes, disintegrates into silicon:

$$_{15}P^{30} \longrightarrow {}_{14}Si^{30} + {}_1e^0 \text{ (positron)} \qquad (10)$$

Sodium bombarded with neutrons turns into radioactive sodium,

$$_{11}Na^{23} + {}_0n^1 \longrightarrow {}_{11}Na^{24} \qquad (11)$$

and this decays, with a half-life of 14.8 hours, to give magnesium:

$$_{11}Na^{24} \longrightarrow {}_{12}Mg^{24} + {}_{-1}e^0 \text{ (beta particle)} \qquad (12)$$

Radioactive arsenic, with a half-life of 26.8 hours, is easily prepared:

$$_{33}As^{75} + {}_0n^1 \longrightarrow {}_{33}As^{76} \qquad (13)$$

A large number (about five hundred) of such artificially radioactive isotopes have now been made.

Manufacture of Elements · In addition to these many artificially radioactive isotopes of elements already known, many new elements, the transuranic elements (lying beyond uranium), have been made. These include the elements neptunium (Np), 93; plutonium (Pu), 94; americium (Am), 95; curium (Cm), 96; berkelium (Bk), 97; californium (Cf), 98; einsteinium (E), 99; fermium (Fm), 100; and mendelevium (Mv), 101. These elements are placed in the periodic table (p. 313) in the *actinide series*, which contains also the previously known elements actinium, thorium, protactinium, and uranium (considered in Chapter 37). The elements beyond atomic number 88 resemble one another very closely in chemical properties and, like the rare-earth elements, probably belong to Group IIIA.

Neptunium and plutonium are made in small amounts by the reaction of high-speed deuterons, from the cyclotron, with uranium. They are formed also as a result of a sequence of reactions starting with the capture of a neutron by the nucelus of U^{238}. The U^{239} thus formed is radioactive (with a half-life of 23 minutes) and loses a beta particle to form neptunium, which (with a half-life of 2.3 days) in turn loses a beta particle to give an atom of plutonium (which decays, with a half-life of 24,000 years, giving off alpha particles). The sequence of results is represented as follows:

$$_{92}U^{238} + {}_{0}n^{1} \longrightarrow {}_{92}U^{239} + \text{gamma rays} \quad (14)$$

$$_{92}U^{239} \longrightarrow {}_{93}Np^{239} + {}_{-1}e^{0}\ (\text{beta}) \quad (15)$$

$$_{93}Np^{239} \longrightarrow {}_{94}Pu^{239} + {}_{-1}e^{0}\ (\text{beta}) + \text{gamma rays} \quad (16)$$

By similar nuclear reactions between $_{2}He^{4}$ and the successively heavier nuclei of the actinides as they are created, next higher members of the series have been created. Three other elements, *technetium* (43), *astatine* (85), and *promethium* (61), have been made by the particle-bombardment technique.

These were missing from earlier versions of the periodic table, and the authenticity of their existence was in such doubt that it was desirable to have them available in larger amount for a study of their properties.

Bombardment of Nuclei in Giant Cyclotron · Bullet-particles from an average cyclotron knock out at most only two or three particles from a nucleus. But bullet-particles accelerated to enormous velocities in the giant cyclotron in use at the University of California can dislodge from twenty to thirty particles from some nuclei. For example, arsenic ($_{33}As$) has been transmuted down to cobalt ($_{27}Co$) and even to chlorine ($_{17}Cl$). A whole new series of isotopes, tending to be lighter than the stable isotopes, has been prepared. As the study of the smashing of atomic nuclei progresses, we may expect to learn much more than we know now about the manner in which the protons and neutrons are packed together.

Transmutation of Gold into Mercury · While the old alchemists were interested in transmuting mercury into gold, we have found it very much worth while to bring about the reverse change. The mercury produced by transmutation from gold, even in tiny amounts of 50 to 100 mg, is useful in setting up a standard unit of length.

The meter, the arbitrarily defined distance (p. 12) between two marks scratched on a platinum-iridium bar, is accepted as the usual standard of length. But the wave length of the spectroscopic green line of mercury (p. 122) would be a much more precise and convenient unit for many purposes were it not for the fact that ordinary mercury has seven isotopes. Every one of these gives a slightly different line, and the composite line is too broad. But the single isotope of mercury, Hg^{198}, formed by exposing gold, which occurs in nature as a single isotope, Au^{197}, to neutrons

$$_{79}Au^{197} + {}_0n^1 \longrightarrow {}_{80}Hg^{198} + {}_{-1}e^0 \qquad (17)$$

gives a single, very narrow green line, at 5461 Å, the wave length of which is reproducible and measurable to about one part in a billion. The length of this wave of green light bids fair to become our primary unit of length.

Atomic Energy; A-Bomb and H-Bomb

When Hahn and Strassmann, working in Germany, announced, early in 1939, that during their study of the reaction of neutrons with uranium-235 the products were found to contain barium, krypton, and other elements of atomic numbers about half that of uranium, great interest was aroused. Frisch and Meitner suggested that uranium atoms were splitting in two, undergoing "fission." It was shown that the heat liberated was enormous and would amount to several million million calories if as much as 1 g-at. wt of uranium could be made to undergo fission. It was realized that here at last might be the chance to make the old dream of releasing atomic energy come true. Whether it could be made to come true depended on *whether enough neutrons were liberated in an atomic fission* to react with further uranium atoms, and whether the effect could be made to spread in a *chain reaction* throughout a given piece of uranium.

It was reported that German scientists were trying to produce atomic energy for use in a military weapon, and so, beginning in 1940, the race was on. The stakes were high because it seemed very likely that the nation that succeeded first would have the power to end and win the war. Many thousands of American scientists and engineers, under extraordinarily competent leadership, devoted their efforts to the production of atomic energy on a large scale—with what amazing and fantastic success all the world has known since two atomic bombs were dropped on Hiroshima and Nagasaki in August, 1945. The fascinating story of the scientific aspects of the whole project was released in a book.* Since that time the hydrogen bomb, or fusion bomb, has been made.

Atomic Energy by Fission and by Fusion · We know that mass may be converted into energy, in accordance with Einstein's equation, $E = mc^2$. But we should like to have something more than the bare equation, a theory if possible, to help us to understand what may happen inside the nucleus when energy is released by the fission of large

**Atomic Energy for Military Purposes*, by H. D. Smyth, Princeton University Press.

atoms, such as uranium-235, and the fusion of small atoms, such as hydrogen (and neutrons). We can get some satisfaction from a consideration of the theory of the *mass defect* and *binding energy.*

Mass Defect · Since we know the number of protons and neutrons in the nucleus of every atom (p. 37), or rather let us say the number of hydrogen atoms and neutrons that go to make up every neutral atom, and since we also know the mass of a hydrogen atom, 1.00813, and the mass of a neutron, 1.00897, we might expect that we could calculate the mass of any atom by simply adding up the masses of the hydrogen atoms and the neutrons contained in it. For example, the mass of the helium atom $(2\,H + 2\,n)$ should be $(2 \times 1.00813) + (2 \times 1.00897) = 4.03420$. But actually the mass of the helium atom is only 4.00386. The difference, $4.03420 - 4.00386 = 0.03034$, is called the *mass defect.*

There is a similar mass defect for every atom; and in order to make a comparison of the mass defects over the whole range of atom masses— light, medium, and heavy— let us plot in Fig. 21-4 A the mass defect per

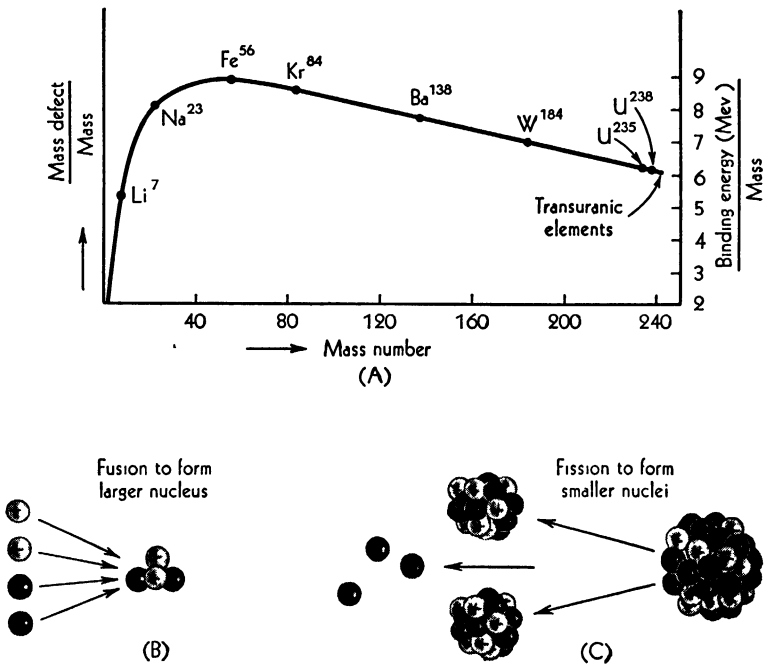


Fig. 21-4. Mass Defect and Binding Energy · The curve in A shows the trend of mass defect per unit mass, as well as the binding energy (in millions of electron-volts, Mev) per unit mass, both as the mass number increases. The energy that binds together these *nucleons,* the protons and neutrons, in the nucleus is tremendous. One electron-volt is 1.6×10^{-19} joules, or $6.02 \times 10^{23} \times 1.6 \times 10^{-19}$ joules for one mole of electrons; and 1 Mev is 1 million times this quantity

unit mass (mass defect divided by mass number) against mass number. It will be noted that the mass defect is greatest for iron, Fe, clearly at the crest, and that the curve falls away sharply toward the lighter elements and gently but definitely toward the heavier ones.

Binding Energy and Stability of Nuclei · We theorize that the loss in mass occurred for all the atoms long ago, perhaps several billion years ago, when they were being formed originally from hydrogen atoms and neutrons; that mass was converted to energy which was liberated at that time, in accordance with the equation $E = mc^2$, as hydrogen atoms (or protons) and neutrons fell together and packed closely under the extremely strong attractive forces between them.

The energy liberated is called *binding energy*, by analogy with the chemical energy of the binding together of atoms like carbon and oxygen in the exothermic chemical reaction forming carbon dioxide. In general, the greater the binding energy, the greater the stability of the union, whether of chemical atoms or of nuclear particles. Since binding energy is proportional to mass defect, the curve of Fig. 21-4 A also illustrates binding energy per unit mass.

Present Source of Atomic Energy · Clearly, then, supposing that our theory holds good, we can obtain energy for ourselves from the nuclei of the atoms by two different general methods. (1) We can in some way induce the nuclei of the lighter atoms, far to the left in Fig. 21-4 A, to fuse together, thus moving *up* the curve to form more stable, heavier atoms containing more tightly packed nuclear particles, and thereby liberating the energy that comes from closer packing. This is shown in Fig. 21-4 B by the fusion of $2\,H + 2\,n$ to form He. (2) We can, on the other hand, induce any of the heavy atoms, at the extreme right (Fig. 21-4 A) to split or undergo fission (Fig. 21-4 C) into lighter but more stable atoms, again moving *up* the mass-defect curve toward the crest (Fe), and again liberating energy that comes from closer packing.

The working out of method 2 came first, through the fission of uranium-235 and of plutonium, and we shall discuss it first. Then we shall return to method 1, giving energy by fusion.

Fission of Uranium · The uranium isotope U^{235} undergoes fission when bombarded by neutrons. In uranium this isotope is mixed with U^{238} in the ratio 1 to 140. Since the much more abundant atoms of U^{238} interfere with the fission of U^{235} atoms by neutrons, it is necessary to remove at least some of the U^{238}, or to concentrate the U^{235}. This is done by first converting natural uranium into the hexafluoride, UF_6, a compound volatile enough to be handled as a vapor. Then the vapor is allowed to diffuse through a specially prepared barrier. The diffusion

follows Graham's law (p. 73); and although the difference in mass between the hexafluorides of U^{238} and U^{235} is slight (352–349) and the proportion of U^{235} small to start with, it is possible, with a large number of diffusion stages, to achieve the desired concentration. Uranium-235 is concentrated also in a machine that is virtually a large mass spectrometer (p. 142); and it can be concentrated in other ways. The uranium hexafluoride is converted to metallic uranium for use in the atomic bomb and in nuclear reactors.

The U^{238} nucleus also may capture a neutron; but then, instead of fission, several successive nuclear reactions, represented by equations (14), (15), and (16), occur, and plutonium is produced. *Plutonium* will undergo fission on neutron capture, in very much the same manner as uranium-235.

The Chain Reaction · When an atom of uranium-235 absorbs a neutron and undergoes fission, it splits, on the average, approximately but not exactly into equal halves. In fact, about 300 isotopes, most of them radioactive, are produced, the atomic numbers of the products ranging from 30 for zinc to 64 for gadolinium, and mass numbers from 72 to 162; though about one fourth of the total mass is found in a few elements grouped around barium and another fourth around krypton. Free neutrons are also produced, since there are relatively fewer neutrons in the light elements than in the heavy ones. That the number of neutrons exceeds the number of protons to a greater extent in the heavy nuclei than in the light nuclei has already been stated (p. 37); and the extent of the excess is obvious, of course, for any atom from a comparison of the mass number and the atomic number of the atom. For example, the numbers of neutrons and protons in the following nuclei are, respectively, 2 and 2 in ${}_2He^4$ (excess of neutrons = 0); 6 and 6 in ${}_6C^{12}$ (excess of neutrons = 0); 48 and 36 in ${}_{36}Kr^{84}$ (excess of neutrons = 12); 82 and 56 in ${}_{56}Ba^{138}$ (excess of neutrons = 26); 143 and 92 in ${}_{92}U^{235}$ (excess of neutrons = 51); 145 and 94 in ${}_{94}Pu^{239}$ (excess of neutrons = 51).

If, then, ${}_{92}U^{235}$, in undergoing fission, splits up to give, say, ${}_{36}Kr^{84}$ and ${}_{56}Ba^{138}$, the 92 protons are divided into the portions 36 and 56; and if the 143 neutrons are divided into the portions 48 and 82 (a total of 130), there are 13 free neutrons left over. However, some of the isotopes keep some of these neutrons, and only, on the average, about 2.5 free neutrons are liberated by the fission of U^{235}. But these are the ones that are responsible for the propagation of the fission reaction throughout a quantity of U^{235}. Each uranium atom undergoing fission bombards its neighbors with neutrons; these in turn undergo fission and bombard their neighbors, and so on, so that a chain of fission reactions is produced.

Summarizing Statement about Release of Energy by Fission · The fission of the heavy nucleus U^{235} (and $_{94}Pu^{239}$), by the capture of a neutron, not only liberates energy, because the nuclei of the fission products have larger mass defects than the original heavy nucleus, but also liberates neutrons, which cause fission in other nuclei of U^{235}, thus giving the chain reaction.

Further, it should be noted that neutrons pass very freely and easily through all matter, even through a piece of metallic uranium—in fact, so easily that the neutrons fail to set up an effective chain reaction (because they escape through the surface of the piece of uranium) unless the piece has a certain minimum volume, a certain *critical size.*

Atomic Bomb · Many atomic bombs have been set off: the experimental bomb at Alamogordo, in the New Mexican desert; the bombs over Hiroshima and Nagasaki; the two bombs of the Bikini tests, Test Able and Test Baker. Tests have been made also at Eniwetok; and there have been many tests on the desert at Yucca Flats, Nevada, said to have led to an improvement in power of 25 times over that of the Hiroshima bomb.

If, when an atomic bomb is set off, as much as 1 g of mass is converted into energy, the quantity of energy produced, as calculated from Einstein's equation, should be 9×10^{20} ergs, or about 21.5 million million cal (p. 19), equivalent to the heat of combustion of 2500 tons of the best coal. It has been estimated that the energy of the atomic bomb is liberated in less than one millionth of a second, and that the temperature attained is of the order of 100,000,000 degrees. There is no wonder, then, that the bomb is so devastating in its effects.

The bomb has several effects. At Hiroshima and Nagasaki the blistering heat burned combustible substances up to distances of 1.5 miles from the center of explosion. The mechanical shock, or blast, was said to have been as great as that of an explosion of 20,000 tons of TNT, and able to exert a pressure of concussion of about 6 tons/sq ft against a stone or concrete wall about 0.5 mile distant. Such a pressure is more than 100 times greater than that produced by the most violent hurricane. There was an instantaneous emission of strong gamma radiation that penetrates even concrete walls and that is lethal or very seriously damaging to human beings at distances of 0.5 to 1.0 mile. At Test Able, where a bomb was set off high above a fleet of anchored ships, five ships were sunk and others were seriously damaged in an operation which, in time of war, would be a major naval disaster. At Test Baker, where a bomb was set off about 60 ft under water, the damage to ships was even greater; and a column of water, estimated to contain about 10,000,000 tons of water, was

raised into the sky. Caught in such a rising column of water, a battleship weighing 40,000 tons would be like a chip of wood in a fountain.

When a bomb is exploded in the air, well above a target, the intensely radioactive fission products seem to be carried by the billowing "mushroom" cloud many miles upward from the explosion. They are scattered and diluted in the immense expanses of the upper atmosphere so completely that little, if any, harm ever results from these dangerous products. But if a bomb is exploded under water, the radioactive products are largely trapped in the water; and if a bomb is set off in lake, river, or coastal-harbor waters adjoining densely populated areas, the contaminated water that will probably be splashed and spattered over such areas can not only wreak havoc among the people living there, but also render the areas unfit for human habitation for years.

Radiation Damage to Human Beings · All the radiations (alpha, beta, and gamma rays, and neutrons) from radioactive substances have been shown to cause damage to animal tissue. Particularly dangerous are the violently active gamma and neutron radiations, which penetrate deeply into tissue, and affect it in many ways. They may produce burns similar to sunburn, but much deeper and more severe; they may destroy some of the genes and cell chromosomes, and thus cause mutations, or new types of cells, to develop; more frequently they reduce the number of white blood cells by destroying or severely restricting the reproductive powers of the cells that produce them in the bone marrow. This latter effect results in "radiation sickness," and leaves a person susceptible to many kinds of bacterial or virus infections until the white-blood-cell count has been restored.

The Hydrogen Bomb · Certain information about fission energy has been given in the Smyth Report (p. 358). But there has been little if any authentic disclosure of the nature of the liberation of energy of fusion in the "hydrogen bomb."

One reads in the public press that the principal nuclear reaction is the fusion of two atoms of deuterium to form helium, with the production of a very great amount of energy:

$$ {}_1H^2 + {}_1H^2 \longrightarrow {}^1He^4 + \text{Energy} \qquad (18) $$

It is supposed that this reaction is started with great difficulty, but that it can be initiated at the enormous temperature produced in an atomic-bomb explosion. Thus a fission-fusion sequence may be involved. Further, it is supposed that the hydrogen isotope tritium, ${}_1H^3$ (p. 91), reacts much more easily than does deuterium and so may be employed, mixed in suitable proportion, as a "match" to fire the more sluggish

deuterium; or that the compound lithium deuteride, LiD, may possibly be used and transmuted into tritium on the spot.

It will be remembered that the violence of the Hiroshima bomb was said to be comparable to that of 20,000 tons of TNT; and that the improved A-bomb was about 25 times as strong. The H-bomb of March, 1954, is said to have been many times as powerful, equivalent perhaps to 20 megatons, or 20 million tons, of TNT, and correspondingly more violent in (1) blast, (2) thermal effect, and no doubt (3) intensity of radiation.

In addition, a fourth terrifying factor comes upon the scene here, namely the "fall-out." It is said that at Bikini the fall-out, which was radioactive slaked lime (CaO) produced by the blasting of the coral ($CaCO_3$) of the Pacific island, spread out over about 7000 square miles. It caused some damage to human life and to fish.

Among the ashes of the fall-out, Japanese scientists are said to have identified fission products of uranium, and this has led to the guess that the hydrogen bomb was surrounded by a coating or tamper of uranium. The arrangement, then, instead of being fission-fusion would be fission-fusion-fission. Under these conditions it is said that even uranium-238 undergoes fission, and contributes tremendously to the violence of the bomb.

Aside from the manifold direct threats to life, some scientists think that there is also the chance that genetic damage (damage to the genes) may occur, with all the implications that such a thing may have for future generations.

Nuclear Reactor · Nuclear reactors, already mentioned, are essentially tamed bombs. They are of several types, depending upon the substance used as a "moderator." A reactor using graphite as the moderator consists of a rectangular block of graphite provided with slots, into which are inserted metallic rods of natural uranium. The uranium rods are "canned" in a sheath of aluminum to protect them against corrosion by the water which may be used as a cooling agent in the pile. The U^{235} in the metallic rods serves, by fission, as the source of neutrons; but such neutrons have a very high velocity and must be slowed down. It is the function of the graphite, called a *moderator*, to do this. Then the neutrons, slowed by passage through the graphite, are captured by the atoms of U^{238}, and plutonium is formed in a series of nuclear reactions represented by equations (13), (14), and (15). In the process an immense amount of heat is generated. The rate of the reaction may be controlled by varying the amount of uranium inserted in the pile, and also by the insertion of rods of *cadmium* or of *boron steel* (the "control rods") which absorb neutrons.

If the plutonium is to be recovered, the uranium rods are withdrawn and dissolved; and the plutonium is extracted and purified by chemical means. It is reported that all the chemistry of separation and purification was worked out originally with less than 1 mg of plutonium.

Industrial Use of Atomic Energy · It seems likely that such reactors operated to produce heat energy (and plutonium), will be an important source of energy for industrial use—to generate steam in municipal power plants and in other power installations. The plutonium produced might be used in the controlled production of atomic energy, as might uranium-235 and other fissionable substances. The natural thorium atom, ${}_{90}Th^{232}$, will capture a neutron and then emit two beta particles to give ${}_{92}U^{233}$, which, like plutonium, is an artificial fissionable atom.

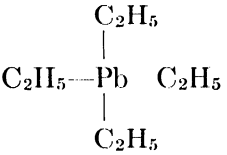
Submarines driven by nuclear reactors have been constructed, and several countries have permanent installations on land (see Chapter 47). One of the problems involves adequate protection against the radiations which arise from the reactor.

Many radioactive isotopes, fission products, and disintegration products are formed during the operation of a reactor; and various elements may be introduced into it so that they may undergo nuclear reactions of various sorts with the neutrons which are produced in large quantities. Many of these radioactive isotopes now find an extensive use in university and industrial research as "radiotracers."

Radiotracers

Atoms that are radioactive can form compounds and enter into chemical reaction in the usual way. Such atoms are "tagged" and are called *radiotracers*. They show their presence by the radiations which they send out. What they do in a reaction and where they go in a process can be followed, or *traced*, with an electroscope (p. 321) or preferably with a more sensitive instrument, the Geiger counter (p. 80). It will be shown, on pages 438–439, how radioactive arsenic (a radiotracer) can be used to demonstrate the truth of a certain theory that chemists had for a long time believed to be true but had never been able to prove experimentally, namely, that even after equilibrium is attained in a chemical reaction, the forward and the reverse reactions continue to occur. The rapid development of the application of radiotracers in the study of various phenomena is bringing results that shed new light on the details of the mechanism of chemical processes. From the many hundreds of possible illustrations let us select a few.

The difference in the nature of covalent and electrovalent compounds we already understand. The difference has been shown dramatically in the following way: Some crystals of lead nitrate ($Pb(NO_3)_2$) made from radioactive lead (radium D), together with some crystals of ordinary lead chloride ($PbCl_2$), were dissolved in water. When the solution was evaporated, the crystals of the two compounds reappeared; but the crystals of lead chloride also were then radioactive, which showed that lead ions (Pb^{++}) were free and that some of them that were originally associated with nitrate ions (NO_3^-) had paired off with chloride ions (Cl^-). However, if tetraethyl lead,



a covalent compound, is made from radioactive lead and shaken with a solution of lead chloride, the lead atoms do not leave the tetraethyl lead. They are held firmly bound to the ethyl groups by covalent bonds.

The use of radiotracers is not new. The experiment just described was done long ago, before the time of the atom-smashing machines, with a *natural* radioactive element. But today we are not restricted to the use of the natural radioactive elements since all the elements, including the light elements, so important in chemical processes, can now be made radioactive. The field of usefulness of radiotracers is greatly extended.

In Engineering · An interesting application of the tracer technique involves the measurement of the wear of the piston rings in an automobile engine. Such rings, pictured in Fig. 33-20 (p. 596), clasp the piston in grooves and improve the closeness of its fit against the cylinder walls. One of the functions of the lubricating oil in the engine is to form a film of oil on the inside walls of the cylinder and to reduce the friction and the wear of metal as the piston moves up and down. To measure the amount of wear by determining the amount of fine metal powder rubbed off and accumulated in the oil requires a long running time and is a difficult task. But if the iron rings are irradiated with neutrons in a reactor and some of the atoms in the iron have thus become radioactive, the oil that is to be tested for its effectiveness as a lubricant may be examined for radioactivity as the test proceeds. Using a scintillation counter, significant measurements of wear can be made after a running time of about half an hour.

In Biology · The compound penicillin contains sulfur, and *radiopenicillin* has been produced by adding radiosulfur to the material on

which the penicillin-producing mold is grown. It is being used to determine how much penicillin is in the blood at any time after the administration of a dose, how fast it is excreted from the body, whether some organs store more than others, and perhaps to solve the problem of how penicillin stops or kills disease germs. With radiopenicillin and with the possibility of making streptomycin (p. 568) and other antibiotics radioactive, scientists hope to obtain very important knowledge of this sort much more quickly and easily than by strictly chemical methods—which often are not feasible anyhow.

A compound containing radiophosphorus has been fed to rats, and it has been shown that there is a constant reconstruction of bone tissue; the atoms of phosphorus remain in bone for about a month, on the average, before they are replaced. Radioactive carbon ($_6C^{14}$) is usually prepared in the uranium pile by the bombardment of nitrogen atoms (in ammonium nitrate or in calcium nitrate) by neutrons:

$$_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{14} + {}_1H^1 \qquad (19)$$

It has been made up into various carbon compounds, including radioactive carbon dioxide; and many interesting and important reactions and processes, among which is photosynthesis, are being studied.

By the same reaction (equation 19) with neutrons, produced by cosmic rays in the upper atmosphere, nitrogen is transmuted into C^{14}, which is oxidized to carbon dioxide. The radioactive carbon dioxide is being formed constantly; it mixes with ordinary carbon dioxide and is assimilated in photosynthesis. It is present in all living matter to an extent which is related to its constant concentration in the atmosphere.

In whatever compounds or materials the C^{14} may be present it disintegrates, and its half-life is 5568 ± 30 years. A specimen of formerly living material—if it might happen to have been preserved by isolation, as by burial underground—or its carbonaceous remains, would have been steadily losing its carbon-14 activity, perhaps over a period of many thousands of years. A sensitive counter may be used to measure the activity that is left, and from this the age of the specimen may be calculated.

It is certain that with the aid of radiotracers much more rapid progress will now be made in our understanding of many of the complex changes that occur in life processes, the mechanism of the chemical reactions, the physiology of plants and animals, the nature of growth and disease, and perhaps the explanation of aging and death. The United States Atomic Energy Commission is making many of the important radiotracers available, at very small cost, to the research scientists of this country and of

foreign lands so that these fascinating and revealing investigations may be encouraged to the utmost.

QUESTIONS

1. (*a*) What is the nature of the alpha, beta, and gamma rays emitted during radioactive disintegration? (*b*) How may these three rays be detected and distinguished?

2. What general ideas about the structure of atoms result from a study of radioactivity?

3. Explain how charged particles, such as protons and deuterons, are brought to very high speeds in a cyclotron.

4. Write the nuclear equations for the production of helium from the two isotopes of lithium.

5. Give an example of a reversible nuclear reaction.

6. (*a*) Where and how can neutrons be obtained? (*b*) What is the unique advantage of using neutrons for the bombardment of atomic nuclei?

7. How may the following transmutations be brought about? (*a*) Aluminum into silicon; (*b*) sodium into magnesium; (*c*) nitrogen into boron and helium.

8. (*a*) Which are the elements of the actinide series? (*b*) How may neptunium and plutonium be made?

9. Explain the importance, in the development of the atomic bomb, of the action of neutrons (*a*) on uranium-235; (*b*) on uranium-238.

10. Uranium-235 is present to the extent of only 0.71 per cent in natural uranium. Why could not a bomb be made of natural uranium by using a sufficiently large amount of it?

11. Can you give examples, other than those mentioned in this chapter, of the use of radiotracers in chemistry, medicine, agriculture, or industry?

12. What is the artificially made element whose compounds were the first to be prepared in weighable quantities?

PROBLEMS

1. Calculate the mass defect (*a*) for helium; (*b*) for sodium; (*c*) for tungsten-184.

2. The half-life of radium is 1590 years. How long a time will be required for seven eighths of a given quantity of radium to disintegrate?

3. The half-life of carbon-14 is 5568 years. After how long a time will (*a*) all but one fourth of the C^{14} have disintegrated; (*b*) all but one sixteenth?

4. (*a*) Using the Einstein equation, calculate the quantity of energy (in ergs) liberated by the transformation of 5 g of matter into energy. (*b*) Express this quantity of energy in calories. (*c*) How many tons of high-grade bituminous coal would be required to produce the same quantity of heat energy?

CHAPTER 22

THE SULFUR FAMILY

Introduction · The elements oxygen, sulfur, selenium, and tellurium, in Group VIB of the periodic table, constitute a family whose atoms are characterized by the presence of 6 outer electrons. These atoms differ in nuclear charge, in size, and in the number of inner electron shells.

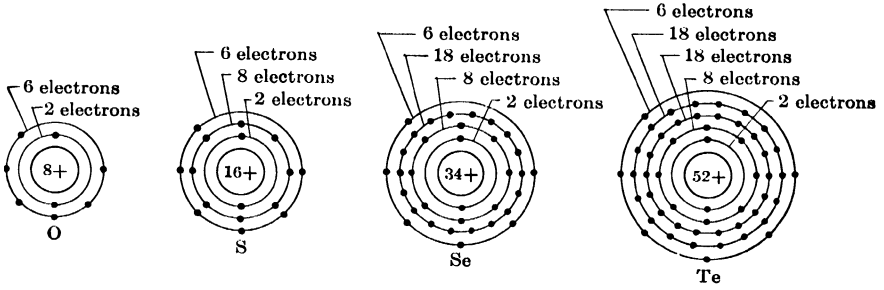


Fig. 22-1. Diagrams Showing the Distribution of Electrons in the Atoms of the Members of the Sulfur Family

As has been shown in Chapter 20, the firmness with which the outer electrons are held increases with increasing nuclear charge, but is diminished as the distance from the nucleus and the number of inner electron shells increase. Since the two latter effects predominate, it may be predicted that the electrons are most tightly held by the oxygen atom and are most loosely held by the tellurium atom. This assumption accounts for and is in accord with the systematic variation in physical and chemical properties which these elements show.

The elements of the family readily form compounds or ions by sharing or adding 2 electrons, provided by atoms of other elements, to complete the octet of the inert-gas structure, thereby acquiring an oxidation state of -2. This tendency is most pronounced in the case of the smallest atom, that of oxygen, and least in the case of the largest atom, that of tellurium. In addition, the atoms of sulfur, selenium, and tellurium may lose (or share) their valence electrons so as to acquire oxidation states up to $+6$. Oxygen does not show this tendency, because its electrons are so tightly held that no other element, with the possible exception of fluorine, is able to remove them. For this reason oxygen is usually studied separately, while sulfur, selenium, and tellurium are considered together. It is well to remember that there are similarities between oxy-

gen and the other elements of the group when they are in the oxidation state of -2. Compounds containing these elements in the oxidation state of -2 are good reducing agents. In the higher oxidation state of $+6$ they are good oxidizing agents; and in intermediate states they may be either. The element polonium, which belongs to this family, is of interest primarily because of its radioactivity and was considered in connection with other radioactive elements.

From the foregoing discussion one may readily understand why the properties of sulfur, selenium, and tellurium vary from the decidedly nonmetallic nature of sulfur to the mildly metallic character of tellurium. For example, the free element sulfur is a nonconductor of electricity. Selenium is a poor conductor; tellurium is somewhat better.

A similar gradation in properties may be seen in the compounds of these elements. Thus, sulfuric acid is a relatively strong acid, selenic acid is not so strong, and telluric acid is weak. The hydrides, H_2S, H_2Se, and H_2Te, are increasingly unstable in that order.

History and Occurrence · Sulfur occupied a prominent place among the few elements known to the ancients, and played an important part in the older views concerning the composition of matter. It is the *brimstone* of the Bible.

Free sulfur occurs in many parts of the world, including Sicily, Japan, Spain, Iceland, and Mexico, as well as in different localities in the United States, especially in Texas and Louisiana. Also, large quantities of sulfur occur in nature in the compounds known as sulfides and sulfates. Some of the most important of these are the sulfides galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and pyrite (FeS_2), and the sulfates gypsum ($CaSO_4 \cdot 2\,H_2O$), barite ($BaSO_4$), celestite ($SrSO_4$), and Epsom salt ($MgSO_4 \cdot 7H_2O$).

Tellurium was discovered by Reichenstein and Klaproth toward the end of the eighteenth century. The latter investigator gave to the element the name it now bears (from a Latin word meaning "the earth"). A few years later (1817) Berzelius isolated a new element, which he named *selenium*, from a Greek word meaning "the moon." Both these elements occur in nature in the free state, as well as in the combined condition, but only in small quantities, far less abundantly than sulfur.

Tellurium is frequently found combined with metals, especially gold, silver, lead, and bismuth, forming compounds known as *tellurides*. In separating these metals from their ores, considerable quantities of tellurium are often obtained, but no important use has been found for it.

Selenium is frequently found in small quantities in natural sulfur. Combined with metals, it occurs also along with some of the sulfides,

especially pyrite (FeS_2). When sulfur or a sulfide containing selenium is used in the manufacture of sulfuric acid, some free selenium is always found in the flue dust, as well as in the slime collecting in the bottom of the lead chambers; and it was from this material that Berzelius first isolated the element. Occasionally compounds of selenium occur in the soil and are absorbed by certain varieties of plants. Cattle and sheep feeding on these plants are poisoned, and thousands have died from this poisoning. The symptoms have been called blind staggers or alkali poisoning. This is a rare instance of the absorption of mineral matter by plants, with the acquisition of poisonous properties by the plants.

The Free Elements

Production and Mining of Sulfur · In normal times the United States produces about 80 per cent of the world's sulfur. The annual production depends largely upon industrial activity in fertilizers, oil-refining, metal production, and rubber, and also very definitely upon exports of sulfur to Canada. The exports amounted to about 1,479,000 tons in 1950 and about 1,315,000 tons in 1951 (Fig. 22-3). The cheapest and most readily available source of sulfur is the native free sulfur mined by the Frasch process, with about 75 per cent of it coming from Texas and 25 per cent from Louisiana. Of the total production in the United States (about 6,000,000 tons) in 1951, about 5,000,000 tons were elemental sulfur, with about 400,000 and 100,000 tons produced respectively from domestic and imported pyrites, and the rest produced from smelter gases, hydrogen sulfide, and other sources. Since the native deposits give indications of ultimate exhaustion, there is a trend toward recovery of more by-product sulfur.

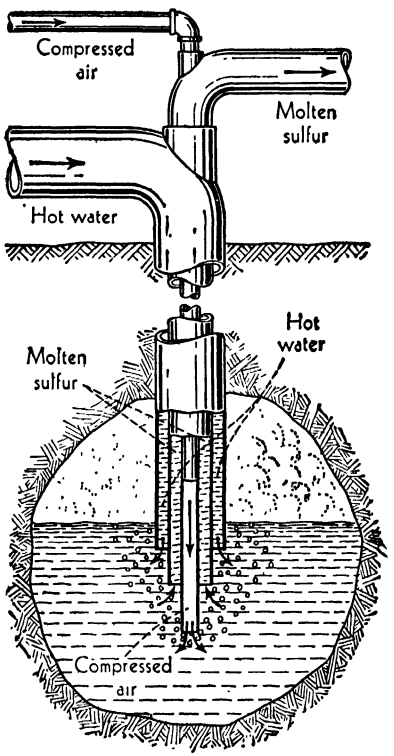


Fig. 22-2. Diagram of the Frasch Process

Frasch process. In Texas and Louisiana the sulfur occurs in large underground deposits covered with quicksand to an extent that makes the ordinary

methods of mining impossible. A typical deposit lies at a depth of about 700 ft, is circular in shape, about one-half mile in diameter, and 500 ft in thickness. The problem of how to get this sulfur was finally solved about 1900 by the American engineer Frasch in a very ingenious way.

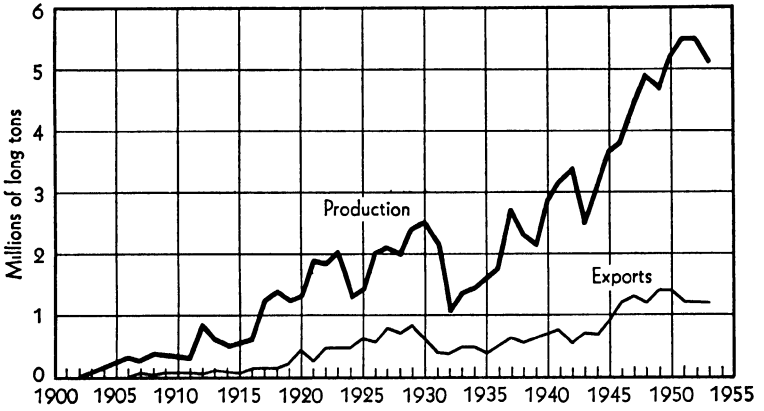


Fig. 22-3. United States Production and Exports of Sulfur, 1900–1953

The principle involved in the Frasch process is shown in Fig. 22-2. A casing is driven down into the deposit, and inside this are placed two pipes, one inside the other. Water heated under pressure to about 170° is forced down between the casing and the adjacent pipe. The sulfur into which the tubes extend is thereby melted (sulfur melts at about 119°). Hot air is also forced down the innermost tube. This bubbles through the melted sulfur at the bottom of the tube, forming a frothy mixture of relatively low density. The pressure of the air and water forces this mixture up through the space between the two inner pipes to the surface, so that a continuous stream of sulfur flows from the pipe, much as the water from a well. A single well has produced as much as 500 tons of sulfur daily, and the product is 99.5 per cent pure. The chief centers of sulfur production in Europe are Italy and Sicily. There the sulfur is melted and drained away from earthy impurities, then distilled from an iron retort, *A* (Fig. 22-4). The sulfur vapor first condenses in the cooling chamber, *B*, in the form of a powder called *flowers of sulfur*. As the chamber becomes warmer, the vapor condenses to a liquid, which is drawn off and allowed to run into cylindrical molds, where it at once solidifies.

By-Product Recovery of Sulfur · In the recovery of sulfur from *pyrite* (FeS_2) the pyrite may be burned in a limited supply of oxygen in such a way that about half the sulfur is distilled off as free sulfur; the rest is oxidized to sulfur dioxide, and then usually converted to sulfuric acid.

From *hydrogen sulfide* sulfur is recovered by first burning part of the sulfide to sulfur dioxide, and then allowing the two gases to react with each other (p. 380).

Properties of Sulfur · Commercial sulfur is a golden-yellow solid which has no marked taste or odor. It is insoluble in water, but its crystalline

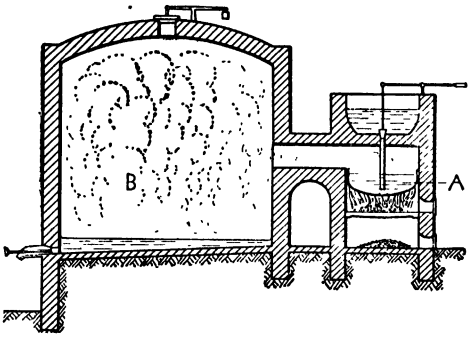


Fig. 22-4. Diagram of a Sulfur Still

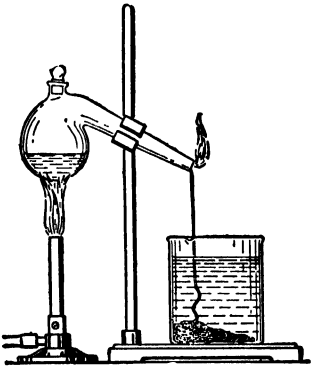


Fig. 22-5. Diagram Representing the Preparation of Plastic Sulfur

forms are soluble in carbon disulfide and in many organic liquids. It melts at 119° into a thin, straw-colored liquid. On further heating, this liquid darkens with increasing viscosity to 200°; then it becomes mobile again but remains dark, and boils at 444.6°. If the hot liquid is suddenly chilled (Fig. 22-5), crystallization is very slow, and it assumes a doughlike form called *plastic* sulfur.

Solid Sulfur · Solid sulfur exists in two distinct crystalline forms.

1. **Rhombic sulfur.** Natural crystals and those deposited from solutions of a solvent such as carbon disulfide (CS_2) belong to the rhombic system (Fig. 22-6). The molecule is made up of 8 atoms (Fig. 22-7).

2. **Monoclinic sulfur.** From the *melted* state sulfur crystallizes in needles belonging to the monoclinic system. These can be most readily observed by melting some sulfur in a small crucible, allowing it to cool and partially solidify, then pouring off the remaining liquid (Fig. 22-8).

These two crystalline modifications differ not only in form, but in most physical constants as well, such as heat of combustion, density, melting point, and vapor pressure (very small).



Fig. 22-6. Crystal of Rhombic Sulfur

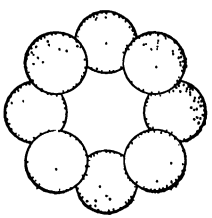


Fig. 22-7. Diagram of a Molecule of Rhombic Sulfur (S_8)



Fig. 22-8. Crystals of Monoclinic Sulfur

When sulfur crystals form below 95.5°, the rhombic variety is obtained, while above that temperature monoclinic crystals result. At this transition point (p. 198) the two forms of crystals remain unchanged when in contact with each other. If heated above 95.5°, the rhombic form gradually changes into the monoclinic form; if cooled below 95.5°, the reverse change occurs:

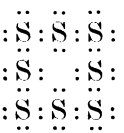
$$\text{Rhombic sulfur} \underset{}{\overset{95.5^\circ}{\rightleftarrows}} \text{monoclinic sulfur}$$

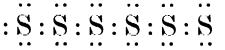
The transition temperature closely resembles the freezing point. The one is the temperature of equilibrium between two solid states; the other, that between a liquid and a solid.

PROPERTIES OF THE CRYSTALLINE VARIETIES OF SULFUR

CRYSTAL FORM	HEAT OF COMBUSTION	DENSITY	MELTING POINT
Rhombic sulfur	69,300 cal	2.07	112.8°
Monoclinic sulfur	69,360 cal	1.96	119.0°

These modifications in the form and internal structure of the sulfur molecules appear to be a result of the tendency of the sulfur atoms, $\ddot{\underset{\ddot{}}{S}}:$, to complete the octet of outer electrons by combining with other sulfur atoms. While the sulfur atoms form diatomic molecules at 800°–1000° like those of oxygen, they form rings and chains at ordinary temperatures.





The viscous form of molten sulfur, called plastic sulfur, is probably a solution of long sulfur chains in molten sulfur.

Properties of Selenium and Tellurium · Selenium, like sulfur, exists in several allotropic forms and an amorphous modification. Gray selenium (a rhombic form) possesses an interesting property: its electrical conductivity, which is very poor in the dark, is greatly increased by light. This property makes selenium useful in the measurement of light intensity—as in measuring the light from distant stars—and in devices for automatically turning lights off in the morning and on at night.

Tellurium exists principally in a rhombic form or as an amorphous material. It has a metallic appearance and possesses many of the properties of the metals.

Chemical Properties of the Free Elements · Sulfur · Sulfur combines directly with most of the elements, metals as well as nonmetals, and the resulting binary compounds are called *sulfides.*

1. **Action upon metals.** Most of the metals, when heated with sulfur, combine directly with it, forming metallic sulfides. Sometimes the action is so energetic that the mass becomes incandescent, as in the reaction of iron with sulfur (p. 23). This property recalls the action of oxygen upon metals, and in general it may be said that the metals which combine readily with oxygen are apt to combine easily with sulfur.

This reaction is a good example of oxidation, since it involves a transfer of electrons from the metal to the sulfur. For example, the reaction of iron with sulfur may be represented thus:

$$Fe + S \longrightarrow Fe^{++} + S^{--}$$

or

$$Fe + \ddot{S}: \longrightarrow Fe^{++} + :\ddot{S}:^{--}$$

2. **Action upon nonmetals.** Under suitable conditions sulfur combines with most of the nonmetals. Thus, with hydrogen it forms the gas hydrogen sulfide (H_2S); with carbon it forms carbon disulfide (CS_2), a heavy, colorless liquid; with chlorine it forms the liquid chlorides, S_2Cl_2, SCl_2, and SCl_4. At ordinary temperatures and in the presence of moisture, sulfur reacts slowly with oxygen, forming sulfuric acid; at higher temperatures it burns, forming the gas sulfur dioxide (SO_2).

3. **Action with oxidizing agents.** When acted upon by oxidizing agents in the presence of water, sulfur is converted first into sulfurous acid and then into sulfuric acid. Since very accurate methods are known for the determination of sulfuric acid, this reaction is the one generally used in estimating the percentage of sulfur present in any substance. It is in such reactions that sulfur differs from oxygen, since, in them, sulfur is acting as a reducing agent, giving up some of its electrons and changing to a higher oxidation state.

Selenium and Tellurium · Selenium and tellurium resemble sulfur in their action with metals, nonmetals, and oxidizing agents, but both their oxidizing and their reducing properties are less pronounced and their reactions less vigorous than those of sulfur.

Uses of the Free Elements · Sulfur is one of the most important raw materials of the chemical industry. About three fourths of the total sulfur, from all sources, is burned and converted into sulfuric acid. Other important uses include those in the vulcanization of rubber, the manufacture of wood pulp, and the preparation of insecticides. The

following table shows the relative tonnage of sulfur used in various industries:

ANNUAL CONSUMPTION OF SULFUR IN VARIOUS INDUSTRIES IN THE UNITED STATES (IN TONS)

Chemicals	1,800,000
Fertilizers and insecticides	750,000
Wood pulp	350,000
Explosives	100,000
Dye and coal-tar products	95,000
Rubber	58,000
Paint and varnish	225,000
Food	8,000
Miscellaneous	200,000

Selenium and tellurium have found no large industrial uses, although some selenium is used in making ruby glass and in neutralizing the green color of glass. Both elements have found some use in hardening alloys.

Hydrogen Compounds

Sulfur, selenium, and tellurium form hydrides, whose formulas are H_2S, H_2Se, and H_2Te. All are gaseous at ordinary temperatures and pressure; the boiling points are $-60.3°$, $-41.3°$, and $-2.2°$ respectively. These gases all have disagreeable odors, and they are all slightly soluble in water. The water solutions are slightly acidic. Because of the relative unimportance of the last two and their similarity to hydrogen sulfide, attention will be directed to hydrogen sulfide.

Hydrogen Sulfide ***(H_2S)*** · Hydrogen sulfide is a gas and is often present in the vapors issuing from volcanoes. Dissolved in water, it constitutes the so-called *sulfur waters* of common occurrence. It is formed when organic matter containing sulfur undergoes decay, and the disagreeable odor attending such changes is often partly due to the presence of this gas. The compound is one of our most important laboratory reagents. It is usually prepared as needed, but it can now be purchased compressed in steel cylinders.

Properties · Hydrogen sulfide is a colorless gas having a mild, disagreeable taste and a very offensive odor. It is 1.18 times as heavy as air. The gas may be condensed to a colorless liquid which boils at $-59.6°$ and solidifies at $-82.9°$. One volume of water at 15° dissolves 4.37 volumes of the gas. By boiling this solution, the gas is all expelled. In pure form it acts as a violent poison and, even when diluted largely with air, it is very dangerous and causes headache, dizziness, and nausea. Fortunately its marked odor gives warning of its presence.

Preparation of Hydrogen Sulfide · This gas may be prepared by the two following general methods:

1. **Synthetic method.** When hydrogen is bubbled through boiling sulfur, some of the gas combines directly with the sulfur to form hydrogen sulfide. The latter is likewise formed when hydrogen is passed over certain sulfides heated to the necessary temperature. These reactions are reversible, as is shown in the following equations:

$$H_2 + S \rightleftarrows H_2S$$
$$4\ H_2 + Fe_3S_4 \rightleftarrows 3\ Fe + 4\ H_2S\uparrow$$

2. **Laboratory method.** Hydrogen sulfide is most conveniently prepared in the laboratory by the action of either dilute sulfuric or hydrochloric acid upon the sulfide of a metal:

$$FeS + 2\ HCl \longrightarrow FeCl_2 + H_2S\uparrow$$
$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S\uparrow$$

Iron sulfide (FeS) is usually employed, although the resulting hydrogen sulfide is not entirely pure. If a greater purity is desired, one may use either sulfide of antimony (Sb_2S_3), which is found in nature in a state of great purity, or sodium sulfide, which can be prepared in the laboratory in a pure condition.

Reason for the reaction. Hydrogen sulfide is very little ionized in solution and is but moderately soluble. Consequently, when an acid is added to a sulfide, the hydrogen ions of the acid and the sulfur ions of the sulfide combine *almost* quantitatively in the equilibrium

$$2\ H^+ + S^{--} \rightleftarrows H_2S\uparrow$$

The water present soon becomes saturated with the gas, which then escapes as fast as formed, and the reaction continues until either the acid or the sulfide is used up (p. 451).

Apparatus. Iron sulfide is placed in a flask, *A* (Fig. 22-9), and dilute acid is added drop by drop from the separatory funnel, *B*. The hydrogen sulfide formed escapes through the tube, *C*, and is collected in cylinders, as shown in the figure.

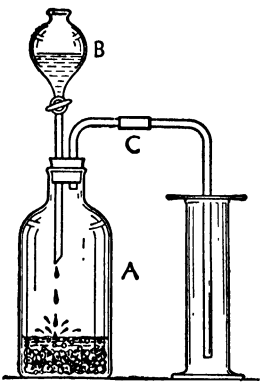


Fig. 22-9. Diagram of Apparatus for the Preparation of Hydrogen Sulfide

Chemical Properties of Hydrogen Sulfide · 1. **Acid properties.** In aqueous solution, hydrogen sulfide is *slightly* ionized. The ionization takes place in two steps:

$$H_2S \rightleftarrows HS^- + H^+ \text{ (primary ionization)}$$
$$HS^- \rightleftarrows S^{--} + H^+ \text{ (secondary ionization)}$$

More ions are furnished by the primary reaction than by the secondary; that is, H_2S is more extensively ionized than HS^-. *This stepwise ionization is characteristic of all acids containing more than one replaceable hydrogen.* The solution of hydrogen sulfide has the general properties of a very weak acid, *hydrosulfuric acid.* It turns blue litmus red and neutralizes bases, with the formation of sulfides.

2. **Action of heat.** Heated to a moderately high temperature, or subjected to the action of electric sparks, hydrogen sulfide is decomposed into its elements.

3. **Action of oxygen.** If a solution of hydrogen sulfide in water (hydrosulfuric acid) is exposed to air, the hydrogen of the sulfide slowly unites with oxygen to form water, while sulfur separates as a solid. In this way are formed the sulfur deposits found about sulfur springs. Hydrogen sulfide is readily inflammable and burns in either oxygen or air, according to the equation

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

When there is not sufficient oxygen to combine with both the sulfur and the hydrogen, the latter element combines with the oxygen, and the sulfur is set free:

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

4. **Reducing action.** Because of the ease with which the sulfide ion gives up two electrons in contact with an oxidizing agent, hydrogen sulfide acts as a strong *reducing agent.* For example, if it is bubbled through concentrated nitric or sulfuric acid, both of which are strong oxidizing agents, the sulfur of the sulfide is oxidized to form free sulfur, and the acid is at the same time partially reduced.

5. **Action upon metals.** The action of hydrogen sulfide upon a number of the metals is very similar to that of water under like conditions, and results in the displacement of its hydrogen by the metal. Thus, when hydrogen sulfide or steam is passed over iron filings heated in a tube, the reactions are as follows:

$$3\,Fe + 4\,H_2S \longrightarrow Fe_3S_4 + 4\,H_2\uparrow$$
$$3\,Fe + 4\,H_2O \longrightarrow Fe_3O_4 + 4\,H_2\uparrow$$

Salts of Hydrosulfuric Acid: Sulfides · The salts of hydrosulfuric acid, the metallic *sulfides*, are an important class of compounds. They are all solids; most of them are insoluble in water, while some are insoluble even in acids. As prepared in the laboratory, some of these salts, such as copper sulfide (CuS) and silver sulfide (Ag_2S), are black; others, as cadmium sulfide (CdS) and arsenic sulfide (As_2S_3), are yellow; while

zinc sulfide (ZnS) is white. Many of these sulfides are found in nature, and some of them are the compounds from which the metals are obtained on an industrial scale. They will be mentioned frequently in connection with the metals. Sulfur combines with many nonmetals, such as carbon and phosphorus, to form sulfides. These are not salts, but are covalent compounds.

Preparation of the Sulfides · The soluble sulfides, like those of sodium and potassium, are most readily prepared by treating the hydroxides of these metals with hydrosulfuric acid. Both the acid and the normal salts may be obtained in this way.

The insoluble sulfides may be prepared by heating the metals with sulfur, although the more convenient method consists in passing hydrogen sulfide into aqueous solutions of metallic compounds. Thus, copper sulfide may be easily prepared by dissolving copper sulfate ($CuSO_4$) in water and passing hydrogen sulfide into the solution. The insoluble copper sulfide precipitates as fast as formed, and may be removed from the liquid by filtration. The reaction which takes place is expressed in the equation

$$H_2S + CuSO_4 \longrightarrow CuS\downarrow + H_2SO_4$$

Oxides and Oxygen Acids

Sulfur forms a number of oxides: sulfur dioxide (SO_2), sulfur trioxide (SO_3), sulfur heptoxide (S_2O_7), and the sesquioxide (S_2O_3). Of these only the first two are of importance; they combine with water to form sulfurous and sulfuric acid respectively. Selenium forms only one oxide, selenium dioxide (SeO_2), a white solid resulting from the burning of selenium in air. It too is an acid anhydride. Tellurium forms tellurium monoxide (TeO), tellurium dioxide (TeO_2), and tellurium trioxide (TeO_3). The two oxides of sulfur are so much more important than any of the others that they merit special discussion.

Sulfur Dioxide (Sulfurous Anhydride) (SO_2) · This is the well-known gas resulting from the combustion of sulfur. It was first obtained in the pure state and recognized as a definite compound by Priestley in 1775. It occurs in nature in the gas issuing from volcanoes and in solution in the waters of some springs.

Properties · Sulfur dioxide is a colorless gas and has the peculiar irritating odor so noticeable when sulfur is burned. It is a heavy gas, 2.2 times as heavy as air. Under standard conditions 1 volume of water dissolves 79.8 volumes of the gas. It is easily condensed to a colorless liquid

that boils at $-10°$ and freezes to a snowlike solid that melts at $-72.7°$. Liquid sulfur dioxide is sold in small steel containers or in tank-car lots for use as a bleach and in some mechanical refrigerators (p. 177).

Preparation · Sulfur dioxide is prepared by the three following general methods:

1. **By the combustion of sulfur or a metallic sulfide.** In either case the sulfur is converted into sulfur dioxide:

$$S + O_2 \longrightarrow SO_2\uparrow$$
$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2\uparrow$$

The enormous quantities of sulfur dioxide used in the manufacture of sulfuric acid are prepared by this general method.

2. **By the action of acids upon a sulfite.** Sulfites are salts of sulfurous acid (H_2SO_3). When an acid, such as hydrochloric acid, is added to a sulfite, sulfurous acid is formed, which decomposes into water and sulfur dioxide. The reactions are expressed in the following equations:

$$Na_2SO_3 + 2\,HCl \rightleftarrows 2\,NaCl + H_2SO_3 \qquad (1)$$
$$H_2SO_3 \rightleftarrows H_2O + SO_2\uparrow \qquad (2)$$

Explanation of the reaction. In the action of hydrochloric acid upon sodium sulfite, as expressed in these equations, we have two reversible reactions depending upon each other. It might be expected that the reaction expressed in equation (1) would be incomplete, since none of the substances represented in the equation is insoluble or volatile in the presence of water. The sulfurous acid, however, decomposes as fast as it forms, according to equation (2), and the resulting sulfur dioxide escapes in the form of a gas. The reaction continues, therefore, until practically all the sodium sulfite has reacted. Since sulfur dioxide is quite soluble in water, it is evident that the reaction should be carried out in the presence of as little water as possible.

3. **By the reduction of sulfuric acid.** Sulfur dioxide may be prepared also by the reduction of hot, concentrated sulfuric acid. This reaction is discussed on page 389.

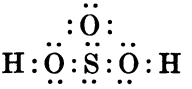
Chemical Properties · Sulfur dioxide is an active substance chemically. It combines directly with chlorine to form *sulfuryl chloride* (SO_2Cl_2); with water to form *sulfurous acid* (H_2SO_3); and with many other substances. Toward oxygen it acts as a reducing agent, being oxidized to sulfur trioxide (SO_3). Toward certain hydrogen compounds it acts as an oxidizing agent, as shown in the following equation:

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

Many *not too stable* oxides of lower valence act in this same way, either as reducing agents or as oxidizing agents. They are oxidizing agents be-

cause they are unstable and give up oxygen readily; they are reducing agents because they tend to take up oxygen and pass to a higher, more stable oxidation state.

Sulfurous Acid (H_2SO_3) · When sulfur dioxide is passed into water, some of the gas combines with water to form sulfurous acid (H_2SO_3),



while the remainder is held in a state of solution. The sulfurous acid formed is in equilibrium, on the one hand with water and dissolved sulfur dioxide, and on the other hand with the ions H^+ and HSO_3^-, resulting from the partial ionization of the acid:

$$H_2O + SO_2 \rightleftarrows H_2SO_3 \rightleftarrows H^+ + HSO_3^-$$

If this solution is heated, it gives off sulfur dioxide and acts as if it were simply a solution of sulfur dioxide in water. Toward a base, on the other hand, it acts as a solution of sulfurous acid, but the acid can be obtained only in the form of a dilute solution. This solution has the following properties:

1. **Acid properties.** In aqueous solutions the compound forms the ions H^+ and HSO_3^-. Some of the latter ions dissociate further into the ions H^+ and SO_3^{--}; the more dilute the solution, the more extensive is this secondary ionization. The solution has all the properties of a weak acid.

2. **Reducing properties.** Sulfurous acid is a good reducing agent; it takes up oxygen either from the air or from unstable substances containing oxygen, and changes into sulfuric acid, thus:

$$2\ H_2SO_3 + O_2 \longrightarrow 2\ H_2SO_4$$
$$H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O$$

In this reducing property it resembles its anhydride (SO_2).

Because of this tendency of sulfurous acid to combine with oxygen, a solution of the acid always contains some sulfuric acid, unless freshly prepared. The speed of the reaction by which sulfurous acid is changed into sulfuric acid is greatly diminished in the presence of a trace of sugar or glycerin, which acts as a negative catalyst (p. 97).

3. **Bleaching properties.** Sulfurous acid acts upon many organic dyes and changes them into colorless compounds. It is therefore useful as a bleaching agent, especially for such substances as paper and straw goods, the texture of which would be injured by a more powerful bleaching agent, such as chlorine.

Illustration. The bleaching properties of sulfurous acid may be shown by bringing a small dish of burning sulfur under a bell jar (Fig. 22-10) in which has been placed some highly colored flower thoroughly moistened with water. The sulfur dioxide combines with the moisture to form sulfurous acid, which slowly bleaches the flower. The reactions involved in these changes are not thoroughly understood. In some cases the sulfur dioxide apparently combines directly with the coloring matter to form unstable colorless compounds. In other cases the bleaching properties seem to be due to the reducing action of sulfurous acid.

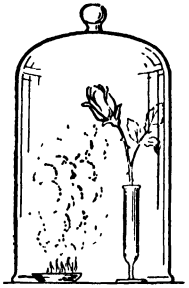


Fig. 22-10. Bleaching a Flower with Sulfur Dioxide

4. **Antiseptic and preservative properties.** Sulfurous acid destroys many microorganisms and may therefore be used as a preservative, to prevent such changes as putrefaction and fermentation, which are caused by these organisms.

Uses of Sulfurous Acid · Sulfurous acid is used mainly in the preparation of sulfites and as a bleaching agent and preservative. Formerly it was often used for disinfecting rooms after the occurrence of contagious diseases, but it is now largely replaced by more effective reagents. Both as a preservative and as a bleaching agent it is used to a considerable extent with certain foods, such as canned corn, dried fruits, sirups, and wines. Whether or not this use should be permitted is a much-debated question.

Salts of Sulfurous Acid: Sulfites · Being dibasic, sulfurous acid forms both acid and normal salts. Thus, with sodium it forms the salts $NaHSO_3$ and Na_2SO_3. With the exception of the sulfites of sodium and potassium, the normal sulfites are either insoluble in water or nearly so, while the acid sulfites are soluble. The normal salts can be prepared either by the action of sulfurous acid upon the hydroxides of the metals or by the general precipitation method used for preparing insoluble compounds. The sulfites are all solid substances and, like sulfurous acid itself, combine readily with oxygen, forming the corresponding sulfates. They are therefore good reducing agents. Because of this property, unless freshly prepared, they are apt to contain some of the corresponding sulfates. Calcium acid sulfite is largely used in the manufacture of paper from wood, since it dissolves the objectionable constituent (lignin) of the wood, leaving the pure cellulose.

Sulfur Trioxide (Sulfuric Anhydride) (SO_3) · Sulfur trioxide is a colorless liquid which solidifies at 16.83° and boils at 44.6°. A trace of moisture causes it to solidify into a mass of silky white crystals. Toward a substance having a strong affinity for oxygen, sulfur trioxide acts as an oxidizing agent, giving up one third of its oxygen and being reduced to

sulfur dioxide. In contact with the air, sulfur trioxide fumes strongly; and it dissolves in water with the liberation of a great deal of heat. The product of this reaction is sulfuric acid; so sulfur trioxide is the *anhydride* of that acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4 + 40{,}470 \text{ cal}$$

Preparation of Sulfur Trioxide · When sulfur is burned in oxygen, minute quantities of sulfur trioxide are formed with the sulfur dioxide. When sulfur dioxide and oxygen are heated together, combination takes place; but the speed of the reaction is so slow that only traces of the trioxide result. In the presence of a catalyst, such as finely divided platinum, the speed is greatly increased; in this way sulfur trioxide can be obtained in quantities. The reaction is reversible, as indicated in the following equation:

$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3 + 2 \times 22{,}200 \text{ cal}$$

The largest yield of sulfur trioxide is obtained when the reaction is carried out at approximately 400°; at this temperature about 98 per cent of the sulfur dioxide combines with oxygen.

Sulfuric Acid (H_2SO_4) · Sulfuric acid has long been known, and was one of the most important reagents employed by the later alchemists. Not only is it one of the most common reagents in the laboratory, but enormous quantities of it are consumed in the industries. It would be hard to name any one chemical compound of more fundamental importance in the arts and industries.

Properties · Pure anhydrous sulfuric acid, or *hydrogen sulfate*, is a colorless, oily liquid. Because of its oily consistency, together with the fact that it was formerly obtained by distilling the (partially oxidized) sulfate of iron known as green vitriol, it is often called *oil of vitriol*. Its density is 1.834 at 20°. When heated to 330° it boils, and a portion of the compound decomposes into sulfur trioxide and water in the process. At a low temperature hydrogen sulfate forms crystals which melt at 10.49°.

Manufacture of Sulfuric Acid · Two general methods for the manufacture of sulfuric acid are in use at the present time. The newer one of these is the *contact* process; the older one is the *lead-chamber* process.

1. **Contact process.** The reactions taking place in this process are represented by the following equations:

$$S + O_2 \longrightarrow SO_2 + 69{,}300 \text{ cal} \quad (1)$$

$$2\,SO_2 + O_2 \xrightarrow{\text{catalyst}} 2\,SO_3 + 2 \times 22{,}200 \text{ cal} \quad (2)$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 + 40{,}470 \text{ cal} \quad (3)$$

These equations, (1), (2), and (3), tell little about the conditions under which the reactions take place. Some of these conditions are as follows.

Sulfur dioxide is prepared according to equation (1), by burning sulfur or some sulfide, such as iron pyrite (FeS_2), in air. The resulting sulfur dioxide, together with sufficient air to furnish the necessary oxygen, is conducted through iron tubes filled with some porous material (asbestos or magnesium sulfate), through which a suitable catalyst is interspersed. The catalyst and its support are kept at about 400°. Under these conditions sulfur trioxide is formed according to equation (2). The resulting sulfur trioxide is then brought into contact with water, with which it unites to form sulfuric acid according to equation (3) (Fig. 22-11).

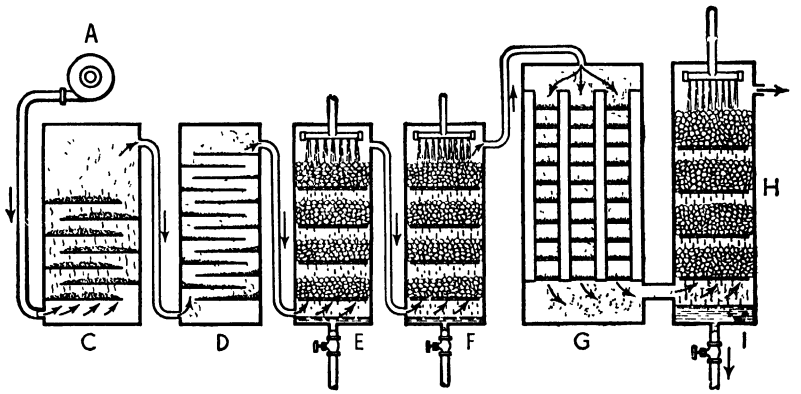


Fig. 22-11. Diagram to Illustrate the Commercial Preparation of Sulfuric Acid by the Contact Process · The sulfur in the chamber *C* is burned by the air forced into the chamber by the blower, *A*. The resulting sulfur dioxide and oxygen (air) are freed from dust by passing through the chambers *D* and *E* and dried by a spray of sulfuric acid in *F*. The gases are then passed over the catalyzer in *G*, where sulfur trioxide is formed by the union of the sulfur dioxide and oxygen. The resulting sulfur trioxide is absorbed in the chamber *H*, by means of concentrated sulfuric acid, and the resulting product is drawn off at *I*

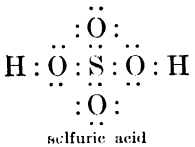
Historical. The only part of the process which is difficult to carry out on a commercial scale is the formation of the sulfur trioxide. It has long been known that sulfur dioxide and oxygen combine when passed over finely divided platinum, but the cost of platinum, together with the poor yield of sulfur trioxide obtained, made the process an impracticable one. A study of the conditions under which the reaction takes place resulted in improvements in the process, until finally, in 1901, the German chemist Knietsch succeeded in overcoming the difficulties to such an extent as to make the process a commercial success for the manufacture of the pure concentrated acid. While platinum is a very effective catalyst for the process, it is very expensive; its commercial value is greater than that of gold. This has led to the use of other catalysts, among which compounds of vanadium and iron oxide appear to be the best.

Some of the more important conditions necessary for making the process a

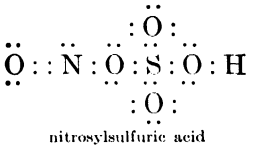
success were found to be the following: (1) The sulfur dioxide and air must be free from dust particles and other impurities, such as the traces of oxides of arsenic which are likely to be formed if iron pyrite or other sulfides are the source of the dioxide used in the process; otherwise the catalyst loses its power. (2) An excess of oxygen over that required in equation (4) must be present. (3) The temperature must be maintained at about 400°. (4) A spray of sulfuric acid containing from 2 to 3 per cent of water must be used for absorbing the sulfur trioxide, since the latter will not combine rapidly with pure water.

2. Lead-chamber process. This process receives its name from the fact that the reactions are carried out in large sheet-lead chambers. The following substances enter into the reaction: (1) sulfur dioxide obtained as in the contact process; (2) a mixture of nitric oxide and nitrogen dioxide; (3) water in the form of steam; (4) oxygen (air). These four substances are introduced in the proper proportions into large sheet-lead chambers, and under suitable conditions they react to form sulfuric acid. The reactions involved are quite complex, and are not thoroughly understood. It is probable that the two following general reactions take place:

a. The substances introduced into the chambers first react to form a derivative of sulfuric acid known as *nitrosylsulfuric acid.* The relation of these two compounds to each other may be seen from their structural formulas:



sulfuric acid



nitrosylsulfuric acid

Nitrosylsulfuric acid differs from sulfuric acid in composition by containing the univalent group (or *radical*) NO (called the *nitrosyl group*) in place of one of the hydrogen atoms of sulfuric acid. Its formation may be represented as follows:

$$2\,SO_2 + NO + NO_2 + H_2O + O_2 \longrightarrow 2\,\begin{matrix} ON{-}O \\ \\ HO \end{matrix}\!\!>\!SO_2 \qquad (1)$$

This acid can be obtained in the form of white crystals called *chamber crystals.*

b. In the commercial manufacture of sulfuric acid, however, these crystals do not form, because the steam changes the nitrosyl acid into sulfuric acid as fast as it is formed:

$$2\,\begin{matrix} ON{-}O \\ \\ HO \end{matrix}\!\!>\!SO_2 + H_2O \longrightarrow 2\,H_2SO_4 + NO + NO_2 \qquad (2)$$

The sulfuric acid collects upon the floor of the chambers in the form of an aqueous solution containing from 62 to 70 per cent of acid. This product is called *chamber acid* and is impure; but for many purposes, such as the manufacture of fertilizers, it needs no further treatment. It can be concentrated by evaporation in open pans made of cast iron, lead, or silica, upon which the acid has little or no action.

It will be noted that in reaction (2) the same quantities of the oxides of nitrogen are formed as are required for reaction (1). Theoretically, therefore, a small amount of these oxides should suffice to prepare an unlimited amount of sulfuric acid; practically, some of the oxides are lost, and this loss must be replaced.

The lead-chamber plant. The simpler parts of such a plant for the manufacture of sulfuric acid are illustrated in Fig. 22-12. Sulfur, or some sulfide such as FeS_2, is burned in the furnace, *A*. The resulting sulfur dioxide, together with the necessary amount of air, passes into the structure *C*, known as the *Glover tower*.

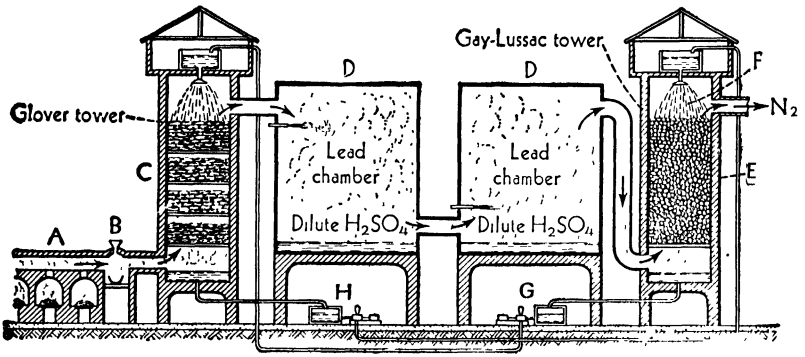


Fig. 22-12. Diagram to Illustrate the Lead-Chamber Process for the Manufacture of Sulfuric Acid

In it the oxides of nitrogen are generated, as will be explained later, and these, together with the sulfur dioxide and air, pass into the chambers, *D*, *D*. Water or steam is also introduced into these chambers at suitable points. Here the reactions take place which result in the formation of the sulfuric acid. The nitrogen remaining after the withdrawal of the oxygen from the air which entered the chambers escapes through the structure *E*, known as the *Gay-Lussac tower*. In order to prevent the escape of the nitrogen dioxide regenerated in the reaction, this tower is filled with pieces of acid-resisting rock or coke over which trickles concentrated sulfuric acid admitted in the form of a spray (*F*) at the top. The concentrated acid absorbs the nitrogen dioxide but not the nitric oxide, so that the latter escapes along with the nitrogen. The acid which is sprayed into the top of the tower collects in the bottom and is run off into the vessel *G*, from which it is forced into the tank at the top of the Glover tower, *C*. Here it is mixed with some dilute sulfuric acid, and the mixture sprayed into the top of the tower,

which is partly filled with some acid-resisting rock. As the acid passes down through this material, it meets with the hot gases entering from the furnace, whereby the nitrogen dioxide is liberated from the acid, passes over into the chambers, *D*, *D*, and again enters into the reaction. During the process just described the dilute acid becomes sufficiently concentrated to serve again as an absorbent of nitrogen dioxide. The necessary quantity of it is therefore run into the vessel *H* from the bottom of the tower, and then forced into the tank at the top of *E*. In order to replace the oxides of nitrogen lost in the process, the necessary quantity is generated in vessel *B*. The sulfuric acid formed collects in the bottom of the chambers and is drawn off from time to time.

Historical. The chamber process dates back to the year 1746. For a number of years previous to this date sulfuric acid had been made by burning sulfur mixed with potassium nitrate in large glass globes. Since these globes were very fragile, and since lead was known to be acted upon to but a very slight extent by the dilute acid, Dr. Roebuck, an Englishman, suggested the substitution of lead-lined chambers for the glass globes. The first plant for the manufacture of the acid by this method was constructed in Birmingham, England.

Relative advantages of the contact process and lead-chamber process. It will be noted that in the contact process it is just as easy to prepare the pure concentrated acid as the dilute acid. In the chamber process the dilute acid is obtained first and can be prepared at a very low cost. It is used almost exclusively in making fertilizers. The operation of concentrating and purifying the dilute acid is expensive, and therefore the contact process is best adapted for the manufacture of the concentrated acid.

By-product sulfur dioxide. The sulfides of some of the metals, such as zinc, copper, and lead, constitute the ores from which these metals are largely obtained. In the extraction of the metals it is often found most convenient first to convert the sulfides into oxides by heating them in the air. The resulting sulfur dioxide may be utilized in the manufacture of sulfuric acid, especially in countries where the cost of sulfur is high. It often happens, therefore, that the manufacture of sulfuric acid is carried on in connection with the separation of metals from their ores.

Radicals · It should be noticed that on page 385 the univalent nitrosyl group, —NO, was called a *radical*; and the question naturally arises, What is the distinction between an ion such as NH_4^+ or OH^- and the univalent radical NO?

In the structural formula for nitrosylsulfuric acid, the NO group is represented as attached to an oxygen atom by a *covalent* bond, whereas ions form electrovalent bonds. We may define a radical as a group of two (or more) atoms *held together* by covalent *bonds*. The same group, such as OH, may act as an ion in one compound (Na^+, OH^-) and as a *combined* radical in others (H—OH or H_3C—OH).

Chemical Properties of Hydrogen Sulfate and of Sulfuric Acid · Pure hydrogen sulfate is a strong oxidizing agent and is extremely corrosive.

When it is heated above 100°, dissociation into water and sulfur trioxide begins. The sulfur trioxide escapes to a greater extent than does the water, until the residual liquid contains 1.67 per cent of water. The resulting mixture then distills at 338° with unchanged concentration (p. 195). If the vapor is heated further, dissociation gradually increases until, at about 450°, it is complete. The reaction is reversible, and recombination of the water and sulfur trioxide takes place as the temperature falls:

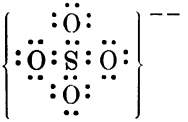
$$H_2SO_4 \rightleftarrows H_2O + SO_3$$

Hydrogen sulfate mixes with water in all proportions, evolves a large amount of heat, and forms sulfuric acid.

The chemical conduct of the acid may be described as follows:

1. **Acid properties.** In concentrated aqueous solutions hydrogen sulfate forms the ions H^+ and HSO_4^-; and the latter, on further dilution of the solution, breaks down into the ions H^+ and SO_4^{--}. It is this aqueous solution containing hydrogen ions which is properly termed sulfuric acid. In a *normal solution* of hydrogen sulfate, 51 per cent of its hydrogen acts as free ions.

The Sulfate Ion · When sulfuric acid ionizes, the sulfate ion is formed. This has a perfectly symmetrical arrangement,



with a double negative charge. Such symmetrical complex ions are very stable, and are quite common in chemistry. Other examples are SiO_4^{----}, MnO_4^-, ClO_4^-, CrO_4^{--}.

2. **Action as an oxidizing agent.** Sulfuric acid parts with one fourth of its oxygen rather easily and, in concentrated form, is a very good oxidizing agent. When heated with metals, sulfur, carbon, or various other oxidizable substances, sulfuric acid acts virtually as though it gave up nascent oxygen according to the equation

$$H_2SO_4 \longrightarrow H_2SO_3 + O$$

3. **Action on metals.** A *dilute solution* of sulfuric acid acts upon the metals that precede hydrogen in the electrochemical series (p. 88) to form a sulfate of the metal and liberate hydrogen. Such a solution has no action upon the metals that follow hydrogen in the series, save as the oxygen of the air first oxidizes the metal.

On the other hand, the *concentrated* acid acts upon a number of the metals without respect to their position in the electrochemical series;

but in all these cases the action results in the reduction of a part of the acid. With copper the equation representing the reaction is

$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2\ H_2O$$

To visualize better the changes which have taken place, the molecular equation may be broken down into an oxidation equation and a reduction equation:

$$\text{Oxidation:} \qquad Cu \longrightarrow Cu^{++} + 2\ e^-$$
$$\text{Reduction:} \quad 4\ H^+ + SO_4^{--} + 2\ e^- \longrightarrow SO_2 + 2\ H_2O$$

Since the same number of electrons is lost in the first equation as is gained in the second, the two electronic partial equations may be added to give the ionic equation

$$Cu + 4\ H^+ + SO_4^{--} \longrightarrow Cu^{++} + SO_2 + 2\ H_2O$$

For a discussion of the various methods for writing and balancing equations which involve a change in the oxidation state of an element see pages 254–259.

4. **Action on salts.** We have repeatedly seen that when a salt of a low-boiling acid is heated with an acid having a high boiling point, the low-boiling acid is liberated from its salt and driven out as a gas or vapor (p. 271). Now sulfuric acid has a higher boiling point than that of any other of the common acids, and, being an inexpensive compound, *it is admirably adapted to the preparation of other acids from their salts.*

5. **Action on water.** When the concentrated acid is mixed with water, a marked contraction in volume takes place. Moreover, the process is attended by the evolution of a large amount of heat, which may even be sufficient to cause the liquid to boil. Care must therefore be taken, in mixing the acid with water, to keep the solution thoroughly stirred during the process, and to pour the acid into the water, not the reverse.

When hydrogen sulfate and water are mixed in molecular proportions —namely, 98 parts by weight of the sulfate to 18 of water— and the resulting solution is cooled, the two unite to form the hydrate $H_2SO_4 \cdot H_2O$. This is a white crystalline substance melting at 8.62°.

6. **Action on organic substances.** Not only can sulfuric acid combine with water, but it will often withdraw the elements hydrogen and oxygen from a compound containing them, decomposing the compound and combining with the water so formed. For this reason most organic substances, such as sugar, wood, cotton and woolen fiber, and even animal tissues, all of which contain much oxygen and hydrogen in addition to carbon, are decomposed by the concentrated acid, leaving the black carbon as a residue.

The Production and Uses of Sulfuric Acid · The annual production of sulfuric acid in the United States fluctuates widely but is more than 10,000,000 tons calculated as 100 per cent H_2SO_4; about two thirds of this is produced by the contact process. The fertilizer industry consumes approximately one third of the output. Large amounts are consumed in the refining of petroleum and products formed in the dry distillation of coal; in the cleaning of scale from iron and steel; and in the manufacture of chemicals. Its minor uses are innumerable.

USES OF SULFURIC ACID IN THE UNITED STATES (TONS OF 100 PER CENT H_2SO_4 ON YEARLY BASIS)		
	Fertilizers	3,500,000
	Iron and steel	590,000
	Petroleum	1,210,000
	Chemicals	2,240,000 (est.)
	Coal products	620,000
	Paints and pigments	670,000
	Rayon and cellulose	650,000
	Explosives	125,000
	Textiles	75,000
	Metallurgy (nonferrous)	325,000
	Miscellaneous	380,000

Salts of Sulfuric Acid; Sulfates · The sulfates constitute a very important class of compounds, and many of them have extensive commercial uses. The normal salts are all solids and, with the exception of those of barium, strontium, and lead, are soluble in water. Two others, namely, calcium sulfate and silver sulfate, are only slightly soluble. The hydrates of many of the sulfates are more frequently used than the anhydrous salts. Some of the more important of these compounds are included in the following table:

SOME COMMON SULFATES		
FORMULA	CHEMICAL NAME	COMMON NAME
$Na_2SO_4 \cdot 10\,H_2O$	Hydrate of sodium sulfate	Glauber's salt
$MgSO_4 \cdot 7\,H_2O$	Hydrate of magnesium sulfate	Epsom salt
$CaSO_4 \cdot 2\,H_2O$	Hydrate of calcium sulfate	Gypsum
$CuSO_4 \cdot 5\,H_2O$	Hydrate of copper sulfate	Blue vitriol or bluestone
$FeSO_4 \cdot 7\,H_2O$	Hydrate of iron sulfate	Green vitriol or copperas
$ZnSO_4 \cdot 7\,H_2O$	Hydrate of zinc sulfate	White vitriol
$BaSO_4$	Barium sulfate	Barite or heavy spar

The sulfates can be prepared by the action of sulfuric acid upon the metals, their oxides and hydroxides, and many of their salts, as illustrated by the following equations:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$
$$Zn(OH)_2 + H_2SO_4 \longrightarrow ZnSO_4 + 2\ H_2O$$
$$2\ NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HNO_3\uparrow$$
$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S\uparrow$$

The insoluble sulfates may be prepared by precipitation. Thus, barium chloride ($BaCl_2$) and sulfuric acid in aqueous solution react as follows:

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2\ HCl$$

The resulting barium sulfate separates in the form of a white solid. Since only soluble sulfates and sulfuric acid yield the ion SO_4^{--} in solution, this reaction serves as a delicate test for these compounds.

Other Oxygen Acids of Sulfur · In addition to sulfurous and sulfuric acids, a number of other oxygen acids of sulfur are known, either in the free state or in the form of their salts. The formulas and names of the most important of these are as follows:

Thiosulfuric acid	$H_2S_2O_3$	Dithionic acid	$H_2S_2O_6$
Hyposulfurous acid	$H_2S_2O_4$	Trithionic acid	$H_2S_3O_6$
Pyrosulfuric acid	$H_2S_2O_7$	Tetrathionic acid	$H_2S_4O_6$
Persulfuric acid	$H_2S_2O_8$	Pentathionic acid	$H_2S_5O_6$

The thionic acids derive their names from a Greek word meaning "sulfur." With the exception of pyrosulfuric acid, these acids are so unstable that they have been obtained only in dilute aqueous solution or in the form of salts. A brief discussion of pyrosulfuric and persulfuric acid follows.

Pyrosulfuric Acid ($H_2S_2O_7$) · Sulfur trioxide dissolves in sulfuric acid in all proportions, forming *fuming sulfuric acid,* often called *oleum.* This acid is of especial importance in the manufacture of dyes. If the sulfur trioxide and sulfuric acid are mixed in molecular proportions, the two combine to form a solid crystalline compound, $H_2S_2O_7$, known as *pyrosulfuric acid.*

Persulfuric Acid ($H_2S_2O_8$) · This acid is sometimes called *perdisulfuric acid* to distinguish it from a similar acid of the formula H_2SO_5, called *permonosulfuric acid* or *Caro's acid.* It will be recalled that in concentrated solutions sulfuric acid is ionized in accordance with the following equation:

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^-$$

When such solutions are electrolyzed, hydrogen is evolved at the cathode. At the anode the ions HSO_4^- are discharged, and under certain conditions the resulting radicals combine to form the compound $(HSO_4)_2$, or $H_2S_2O_8$, which remains dissolved in the liquid about the anode, giving the ions $2\ H^+$, $S_2O_8^{--}$. This compound is known as *persulfuric acid.* While the acid is unstable and exists only in dilute solution, its salts can be obtained in pure condition. They are

prepared by the electrolysis of concentrated solutions of the corresponding acid sulfates. For example, a concentrated solution of potassium hydrogen sulfate, upon electrolysis, yields persulfuric ions at the anode, just as does the electrolysis of sulfuric acid itself.

Oxides and Oxygen Acids of Selenium and Tellurium · Selenium and tellurium form oxides and acids corresponding to those of sulfur. It is of interest that selenious and tellurous acids are more stable than sulfurous acids, while selenic and telluric acids are less stable than sulfuric acid. They are excellent oxidizing agents. It is generally true that, in a family, the more metallic element is more stable in the lower oxidation state.

QUESTIONS

1. Why should water not be poured *into* concentrated sulfuric acid?

2. Suppose you were to heat some sulfur gradually in a test tube until the sulfur was vaporized. State the changes that the sulfur would undergo and the approximate temperature at which each of these changes would take place.

3. In what ways is the transition point between two allotropic modifications of an element similar to the melting point of a pure substance?

4. Why are plants for the manufacture of sulfuric acid frequently located beside lead, zinc, or copper smelters?

5. If one starts with sulfur, how can each of the steps indicated below be effected? Write an equation for each of the reactions which occur.

a. $S \longrightarrow SO_2 \longrightarrow SO_3 \longrightarrow H_2SO_4 \longrightarrow K_2SO_4 \longrightarrow KHSO_4 \longrightarrow K_2S_2O_8 \longrightarrow H_2SO_3 \longrightarrow Na_2SO_3$

b. $H_2S \longrightarrow Ag_2S$

6. (*a*) Draw the electronic diagrams of selenious acid, selenic acid, and the selenate ion. (*b*) What is the oxidation state of selenium in each of these?

7. Complete and balance the following equations by the method of change in oxidation state and by the use of electronic partial equations:

a. $C + H_2SO_4 \longrightarrow CO_2 + ___ + ___$

b. $H_2SO_3 + HNO_3 \longrightarrow H_2SO_4 + NO + ___$

8. Write equations for the preparation of the insoluble sulfides CdS, Ag_2S, and Bi_2S_3 from suitable soluble salts of the metals.

9. Enumerate the uses of sulfuric acid and name the property of sulfuric acid that makes it desirable for each use.

10. *Concentrated* sulfuric acid is often described as an oxidizing acid. Is that true of *dilute* sulfuric acid? Discuss your answer after you have written the electronic partial equations for the following reactions:

$Zn + \text{dilute } H_2SO_4 \longrightarrow$

$Zn + \text{conc. } H_2SO_4 \longrightarrow$

$Cu + \text{dilute } H_2SO_4 \longrightarrow$

$Cu + \text{conc. } H_2SO_4 \longrightarrow$

11. (*a*) Name the insoluble sulfates; the soluble sulfides. (*b*) In a family of elements, how does the solubility of the sulfates vary with the size of the ion? (Choose, for example, the alkaline earths.)

12. Compare the bleaching property of sulfurous acid and that of chlorine.

13. Why does sulfur dioxide not obey Henry's law?

14. Given air, copper, magnesium chloride, sodium chloride, sulfur, water, zinc oxide, and no other substances, show, by writing equations for the reactions involved in all the steps, how you would prepare (*a*) $CuSO_4$; (*b*) $(NH_4)_2SO_4$; (*c*) ZnS; (*d*) $NaHSO_3$; (*e*) $MgSO_4 \cdot 7\ H_2O$.

PROBLEMS

1. Twenty milliliters of a normal solution of sulfuric acid was added to 30 ml of a normal solution of sodium hydroxide, and the resulting solution evaporated to dryness and heated to expel all the water present. (*a*) What substances were present in the residue? (*b*) Calculate the weight of each. (*c*) What substances and how much of each would have been present if 20 ml of a normal solution of sodium hydroxide had been added to 30 ml of a normal solution of sulfuric acid and the same procedure followed?

2. What weight of hydrogen sulfide is necessary in order to precipitate all the cadmium from a solution containing 10 g of cadmium nitrate ($Cd(NO_3)_2$)?

3. (*a*) What weight of iron sulfide is necessary for preparing sufficient hydrogen sulfide to precipitate the copper present in 200 ml of a 0.5 molar solution of copper sulfate? (*b*) What weight of copper sulfide will be formed?

4. A compound was analyzed and found to have the following percentage composition; oxygen, 22.25; sulfur, 11.12; zinc, 22.73; water of hydration, 43.88. (*a*) Calculate the formula of the compound. (*b*) What is the common name of the compound?

5. Calculate from the following data the percentage of hydrogen sulfate in a sample of sulfuric acid: 5 g of the sulfuric acid was dissolved in 100 ml of water and neutralized with a 0.5 *N* solution of sodium hydroxide; 60 ml of the sodium hydroxide solution was required to effect neutralization.

6. If 95 per cent of the sulfur is utilized, what is the daily consumption of sulfur in an industrial plant whose daily output is 200 tons of sulfuric acid containing 98.6 per cent of hydrogen sulfate?

7. (*a*) One hundred liters of hydrogen sulfide will require how many liters of oxygen for complete combustion? (*b*) How many liters of sulfur dioxide will be formed (all gases measured under the same conditions)?

8. What volume of sulfur dioxide, measured under a pressure of 20 lb/sq in. and 120° F, can be prepared by the action of sulfuric acid on 30 lb of sodium acid sulfite?

9. How many grams of concentrated sulfuric acid (H_2SO_4) are required to react with zinc to produce 75 g of zinc sulfate?

CHAPTER 23

THE NITROGEN FAMILY: NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH

The Group · The elements of Group VB form a family whose atoms have 5 outer, or valence, electrons. They differ from one another primarily in the nuclear charge (atomic number), in the number of inner shells of electrons, and in the size of their atoms.

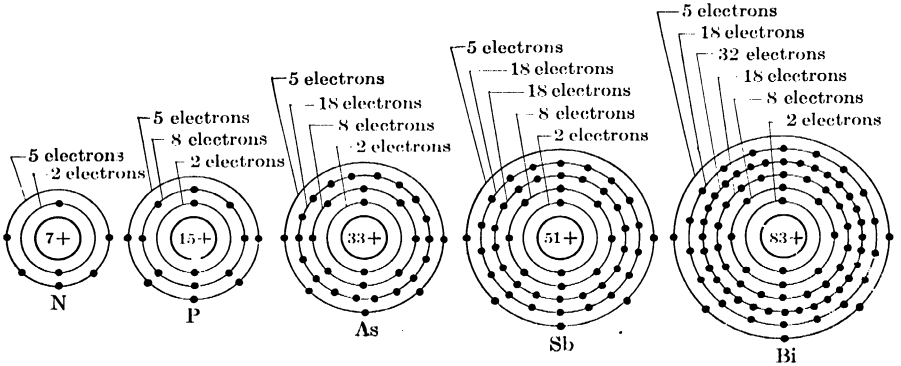


Fig. 23-1. Diagrams Showing the Distribution of Electrons in the Atoms of the Members of the Nitrogen Family

With increasing atomic size the strength with which the outer electrons are held diminishes, both because of their greater distance from the nucleus and because the inner shells of electrons repel them (shielding effect). These effects more than offset the attraction of the larger nuclear charge of the heavier atoms, which, alone, would tend to bind the electrons more closely. This concept, which was discussed at some length in Chapter 20, serves to explain the very interesting gradation of properties, both physical and chemical, from the strictly nonmetallic nature of the type element nitrogen to the wholly metallic nature of bismuth.

These elements have a lowest oxidation state of -3, attained by adding (sharing) 3 electrons to complete the octet. As might be expected from the relative size of their atoms, the tendency to form compounds in this oxidation state is most pronounced in the case of nitrogen. It decreases with increasing atomic size until bismuth forms no stable compound in

which its oxidation state is negative. Thus, ammonia (NH_3) is quite stable, while phosphine (PH_3), arsine (AsH_3), and stibine (SbH_3) are increasingly unstable. Bismuthine (BiH_3) is so unstable that its properties are not well known.

The elements of this group show a maximum oxidation state of +5, corresponding to the 5 valence electrons. They are found also in an oxidation state of +3. As with sulfur compounds, compounds of this family in the lowest oxidation states are reducing, and in the highest oxidation states are oxidizing.

The common oxidation states of an element very often differ by 2. Thus, sulfur shows positive oxidation states of +6 and +4; chlorine, of +7, +5, +3, and +1. This probably arises from the presence of paired electrons, which must both be used, as in a co-ordinate bond.

Since it is generally true that the more metallic properties are found in the lower of the positive oxidation states of any element, and since the more metallic properties are also associated with larger atom size, it is not unexpected (1) that nitric acid is the strongest oxygen acid of the group, (2) that nitrous acid is a much weaker acid, (3) that phosphoric acid is weaker than nitric acid, (4) that antimony hydroxide ($Sb(OH)_3$) may act either as an acid or a base, and finally (5) that the hydroxide of trivalent bismuth is a base.

It may be seen that the elements of this family show a complete transition from the nonmetallic to the metallic state and that this transition is in accord with modern concepts of atomic structure as it influences the physical and chemical properties of the elements.

THE NITROGEN FAMILY

	ATOMIC WEIGHT	DENSITY OF SOLID	MELTING POINT	BOILING POINT	COMPOUNDS WITH HYDROGEN AND OXYGEN
Nitrogen	14.008	1.026	−209.9°	−195.8°	Strong acids
Phosphorus (white)	30.98	1.82	44.1°	280°	Less strong acids
Arsenic (gray) . . .	74.91	5.727	Sublimes	—	Weak acids
Antimony	121.76	6.684	630.5°	1380°	Weak acids and bases
Bismuth	209.00	9.80	271°	1470°(?)	Weak bases and acids

Compounds of Nitrogen

The free *element* nitrogen has already been discussed (p. 105). We shall now consider its compounds in several of its oxidation states, which may vary from −3 to +5.

Hydrides of Nitrogen · Nitrogen forms three important compounds with hydrogen, the names and formulas of which are as follows: *ammonia* (NH_3), a gas, and *hydrazine* (N_2H_4) and *hydrazoic acid* (HN_3), both liquids.

Ammonia (NH₃) · Since ammonia is formed in certain natural processes which are constantly taking place about us, such as the decay of nitrogenous organic matter, it is easy to understand why this compound has been known for so long a time. It was originally prepared by heating the hoofs and horns of animals, and the aqueous solution of the gas so obtained was termed *spirits of hartshorn.* The pure gas itself was first prepared by Priestley in 1774, and its composition was determined soon after by the French chemist Berthollet.

Preparation of Ammonia · Ammonia can be prepared in a number of ways, the most important of which are the following:

1. **Laboratory method.** Ammonia is prepared from an ammonium salt, such as ammonium chloride (NH_4Cl), a colorless salt often obtained in the manufacture of coal gas. When a mixture of ammonium chloride and sodium hydroxide is heated in the presence of a small quantity of water, the ammonium ion combines with the hydroxide ion, as indicated in the following equation:

$$NH_4^+, Cl^- + Na^+, OH^- \longrightarrow Na^+, Cl^- + NH_4OH$$

The resulting ammonium hydroxide (NH_4OH) is unstable and, as fast as it is formed, breaks down into water and ammonia:

$$NH_4OH \longrightarrow H_2O + NH_3\uparrow$$

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

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

Experimental details. The mixture of ammonium chloride and calcium hydroxide is introduced into a flask, *A*, with a little water (Fig. 23-2) and gently heated. Ammonia is evolved and may be collected by bringing the end of the exit tube inside and near the bottom of an inverted bottle, *B*, as shown in the figure. The gas, which is lighter than air, collects in the bottle, gradually forcing the air out at the mouth.

2. **Methods used in industry.** *a. From coal.* Until comparatively recent years nearly all the ammonia used commercially in the United States was obtained as a by-product in the manufacture of coal gas and coke. Certain grades of soft coal contain, in addition to carbon, about 1 per cent of nitrogen and 7 per cent of hydrogen, as well as small percentages

of other elements. When this coal is heated in retorts from which the air is excluded, not only are the combustible gases which constitute coal gas formed, but also ammonia and many other valuable products. From 25 to 50 per cent of the nitrogen in the coal is converted into ammonia, and much of the remainder is set free as molecular nitrogen. The gases expelled from the coal are passed through water, which absorbs the ammonia, together with certain other compounds, forming a solution known as the *ammoniacal liquor*. When this liquor is heated with slaked lime ($Ca(OH)_2$), ammonia is evolved and is absorbed either in water or in a dilute acid solution.

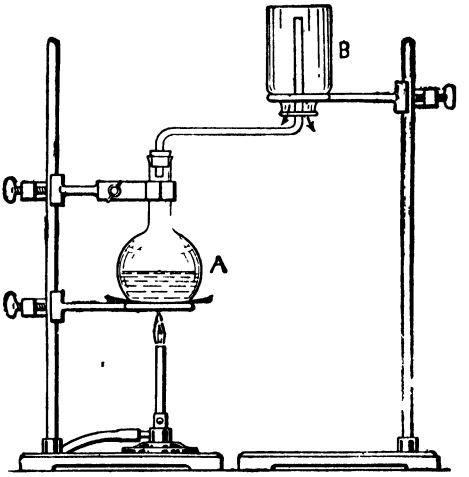


Fig. 23-2. Diagram of Apparatus Used in the Laboratory Preparation of Ammonia

b. By the direct combination of nitrogen and hydrogen (the Haber process). When nitrogen and hydrogen are mixed together in the proportion in which they are combined in ammonia, and the mixture is heated, a small percentage of ammonia is formed, in accordance with the following equation:

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3 + 2 \times 10{,}940\ \text{cal}$$

The low yield is due to the fact that under ordinary conditions the equilibrium expressed in the equation given above is reached when about 2 per cent of ammonia has been formed. The German chemist Haber and his co-workers discovered that this yield could be greatly increased by modifying the conditions of temperature and pressure under which the reaction is carried out and by using a suitable catalyst. The Haber process was developed in Germany under stress of wartime conditions (1914), when the natural sources of nitrogen compounds (chiefly Chile saltpeter, $NaNO_3$) were cut off. This process, or some modification of it, is now the principal one used for the manufacture of ammonia on a large scale.

The conditions for a maximum yield are high pressure and a comparatively low temperature. Thus, the experiments carried on in the Fixed Nitrogen Research Laboratory, maintained by the Federal government at Washington, D.C., show that a yield of 98.3 per cent of ammonia is obtained when the mixture of gases is heated to a temperature of 200° under a pressure of 1000 atm. A great

many catalysts have been used; one of the most effective consists of finely divided iron mixed with a small percentage of potassium aluminate.

Physical Properties · Ammonia is a colorless gas having a strong, suffocating odor. Under standard conditions 1 liter of the pure gas weighs 0.7708 g (0.59 times as heavy as air). Its critical temperature is 132.4°, at which temperature it is liquefied by a pressure of 111.5 atm. Liquid ammonia is colorless and boils at − 33.3°. Its properties were extensively studied by the American chemist E. C. Franklin, who showed that, like water, it is not only an excellent solvent but also a highly ionizing one. At low temperatures ammonia can be obtained in the form of a snowlike solid which melts at − 77.7°.

A noteworthy property of ammonia is its extreme solubility in water. This solution is called *aqua ammonia*. Under a pressure of 1 atm 1 liter of water dissolves 1298.9 liters of the gas at 0°, and 710 liters at 20°. On account of the expansion of the liquid the resulting solutions have a density less than that of water, as is shown in the following table:

DENSITIES OF AQUA AMMONIA

Density	1.00	0.995	0.990	0.980	0.970	0.950	0.930	0.910	0.890	0.880
Per cent by weight of NH_3	0.00	1.14	2.31	4.80	7.31	12.74	18.64	24.99	31.73	35.60

Chemical Properties · Since ammonia is decomposed when heated, liberating free hydrogen, it acts as a reducing agent and reduces certain metallic oxides to the free metal. The hydrogen in the compound readily burns in an atmosphere of pure oxygen, liberating the nitrogen; but combustion will not take place in air unless heat is continuously applied from an external source. Certain metals, such as magnesium and lithium, react with ammonia to liberate all the hydrogen present and form *nitrides*:

$$3\ Mg + 2\ NH_3 \longrightarrow Mg_3N_2 + 3\ H_2\uparrow$$

These nitrides are solids and react with water to form ammonia:

$$Mg_3N_2 + 6\ H_2O \longrightarrow 3\ Mg(OH)_2 + 2\ NH_3\uparrow$$

Sodium and potassium, on the other hand, liberate only a part of the hydrogen:

$$2\ Na + 2\ NH_3 \longrightarrow 2\ NaNH_2 + H_2\uparrow$$

The group NH_2 is termed the *amido* (or *amino*) group, and the compound $NaNH_2$ is called *sodium amide* or *sodamide*. It is a white solid and has important industrial uses.

Like water, ammonia combines directly with certain salts to form *ammonates*, analogous to hydrates. Thus, with calcium chloride it forms the ammonate $CaCl_2 \cdot 8\ NH_3$.

Action of Ammonia with Water · A solution of ammonia in water is basic in character. This property is accounted for by the fact that to some extent hydrogen ions (H^+) leave water molecules to unite with ammonia molecules:

$$H_2O + NH_3 \rightleftarrows NH_4^+ + OH^-$$

When heated, aqua ammonia acts as if it were solely a solution of ammonia in water; for as fast as the ammonia is driven out by heat, the equilibrium existing between the ions represented in the equation is shifted, with the result that more ammonia is formed. If the heating is continued, therefore, all the ammonia is finally driven out. On the other hand, when treated with an acid, aqua ammonia acts as if it were a solution containing hydroxyl ions (OH^-); for as fast as these are neutralized by the acid, more are formed as long as any free ammonia remains in solution. Thus, when hydrochloric acid is added to aqua ammonia, ammonium chloride and water are formed:

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

When the water is evaporated, the ammonium chloride is left in the form of a colorless solid. Similarly nitric and sulfuric acids form, respectively, ammonium nitrate (NH_4NO_3) and ammonium sulfate ($(NH_4)_2SO_4$).

Ammonium Salts · The salts of the univalent ammonium ion (NH_4^+) closely resemble the corresponding salts of the sodium ion in their formulas and chemical properties. Practically all ammonium salts are soluble, which enhances their value as chemical reagents. Small quantities of ammonium salts are found in the soil and in sea water. All the common ammonium salts are colorless solids and may be obtained not only by neutralizing ammonium hydroxide solutions but also by the direct combination of ammonia with the anhydrous acids:

$$2\ NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

When heated, ammonium chloride volatilizes, but is dissociated into ammonia and hydrogen chloride in a reversible reaction:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

A number of other ammonium salts act in a similar way, although some are permanently decomposed by heating.

Ammonium chloride (NH_4Cl) is used in medicine and in making dry cells. It is also used as a flux in soldering and as a chemical reagent. Ammonium bromide and iodide, which are used in photography, closely resemble the chloride, although the iodide readily absorbs moisture upon exposure to air and decomposes to such an extent that the free iodine liberated colors the salt. The fluoride (NH_4F) attacks silicates and is used for etching glass. Ammonium sulfate ($(NH_4)_2SO_4$) and the ammonium phosphates ($(NH_4)H_2PO_4$ and $(NH_4)_2HPO_4$) are important fertilizers, while ammonium nitrate (NH_4NO_3) is a constituent of

certain explosives (*ammonal*). Ammonium sulfide ($(NH_4)_2S$) and carbonate ($(NH_4)_2CO_3$) are important laboratory reagents. Since these two compounds are salts of weak acids with a weak base, they react with water (p. 457). The carbonates of ammonia are used as smelling salts.

Uses of Ammonia · Large quantities of ammonia are used in the manufacture of nitric acid and of aqua ammonia, as well as in the preparation of ammonium sulfate, widely used as a constituent of fertilizers. Gaseous ammonia is used directly as a fertilizer. In the liquid state it is also used extensively as a refrigerating liquid (Fig. 11-12, p. 177.)

Hydrazine (N_2H_4) · This compound may be regarded as having the formula $H_2N–NH_2$. It is composed of two amido groups, just as hydrogen peroxide is composed of two hydroxyl groups (HO· OH). It is a colorless liquid boiling at 113.5°. Like ammonia, it combines with water to form a base from which salts can be prepared by the action of acids. For example, with hydrochloric acid it forms hydrazine hydrochloride, a colorless solid having the formula $N_2H_5^+$, Cl^-.

Hydrazoic Acid (HN_3) · This acid is a colorless liquid of disagreeable odor. It boils at 37°, and the acid, as well as most of its salts, is violently explosive.

Compounds of Nitrogen with Hydrogen and Oxygen · The most important of these compounds are the following:

Hyponitrous acid ($H_2N_2O_2$), a colorless, unstable solid.
Nitrous acid (HNO_2), known only in dilute solution.
Nitric acid (HNO_3), a colorless liquid.
Hydroxylamine (NH_2OH), a white crystalline solid.

The solutions of the first three of these compounds are acids, as is indicated by the names; the solution of the last is a base. Nitric acid will be described first, since it is by far the most important compound of the group.

Nitric Acid · Nitric acid was well known to the alchemists. In the ninth century the alchemist Geber prepared it from saltpeter (KNO_3) by a process somewhat similar to that used in the laboratory at the present time, and the Germans still call it *Salpetersäure.*

Preparation of Nitric Acid · In nature every flash of lightning is attended by the formation of some nitric acid. The electric sparks cause the nitrogen and oxygen of the air to combine to form oxides of nitrogen, which then react with atmospheric moisture to form nitric acid. In 1903 two Norwegians, Birkeland and Eyde, successfully developed this reaction into a commercial process for making nitrates, but the method has been almost entirely abandoned because of the excessive cost of electric power. Two important methods for preparing nitric acid are discussed on the next page.

1. **Laboratory method.** Nitric acid is prepared in the laboratory by the action of sulfuric acid upon sodium nitrate, as indicated in the following equation:

$$NaNO_3 + H_2SO_4 \rightleftarrows NaHSO_4 + HNO_3$$

The reaction is a reversible one, and at ordinary temperatures equilibrium soon results. If, however, a gentle heat is applied to the mixture, the nitric acid is removed as fast as formed, since it has a relatively low boiling point (86°), and may be recovered by condensing the vapors (Fig. 23-3). Under these conditions the reverse reaction cannot take place, and the action between the sodium nitrate and the sulfuric acid continues until it is completed. By heating sulfuric acid and sodium nitrate in a retort under diminished pressure, *pure* hydrogen nitrate is obtained as a distillate.

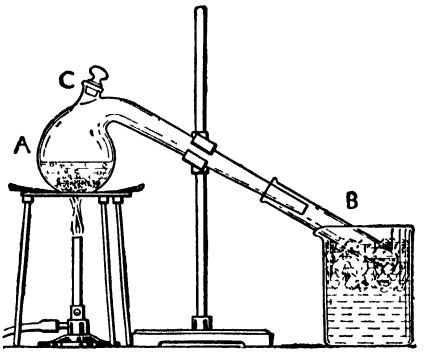


Fig. 23-3. Laboratory Preparation of Nitric Acid Sodium nitrate is introduced into a retort, *A*, and sulfuric acid added. If the retort is gently heated, the nitric acid distills over as fast as formed, and is condensed in a tube, *B*, kept cool by ice water

If double the weight of sodium nitrate indicated in the equation is used, and the mixture is heated to a higher temperature, the sodium hydrogen sulfate which is first formed reacts with the excess of sodium nitrate to form the normal sodium sulfate and nitric acid:

$$NaHSO_4 + NaNO_3 \longrightarrow Na_2SO_4 + HNO_3\uparrow$$

This additional amount of nitric acid is formed without using any additional sulfuric acid. The higher temperature required to bring about the reaction, however, partly decomposes the nitric acid, so that the reaction is not an economical one.

2. **Commercial method: preparation from ammonia.** Inasmuch as the natural supplies of nitrates are limited, many experiments have been carried out in the hope of finding some method of preparing the acid and its salts (the nitrates) from the inexhaustible supplies of nitrogen and oxygen in the air. These experiments have been successful, and the method developed has replaced the older methods entirely. In the new method ammonia is first produced by the Haber process (p. 397) and then oxidized by the oxygen in the air. This last step, which results in the formation of nitric acid, is accomplished by passing a mixture of ammonia and air through tubes or chambers containing a suitable catalyst (Fig. 23-4). Many experiments have been carried out in order to find the most ef-

fective catalyst. Hot platinum gauze seems to be the best, although the much cheaper iron oxide has also been used.

The reactions involved in the process vary somewhat with conditions, but in a general way they may be expressed by the following equations:

$$4\,NH_3 + 5\,O_2 \xrightarrow{\text{catalyst}} 4\,NO + 6\,H_2O \quad (1)$$

$$2\,NO + O_2 \longrightarrow 2\,NO_2 \quad (2)$$

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO \quad (3)$$

The nitric oxide (NO) generated according to equation (1) is again oxidized by free oxygen to nitrogen dioxide (NO_2), as indicated in equation (2). When the process is carried out under atmospheric pressure, the nitric acid formed contains

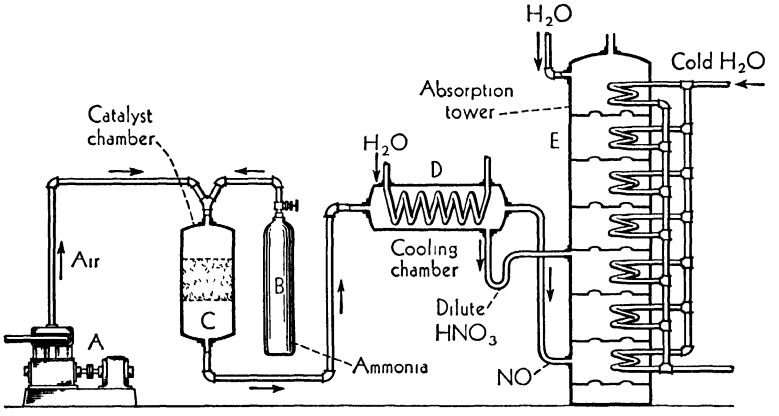


Fig. 23-4. Diagram of the Essential Parts of the Apparatus Used for Preparing Nitric Acid on a Large Scale by the Oxidation of Ammonia · Filtered air, which furnishes the oxygen required for the oxidation of the ammonia, is forced by the pump, *A*, into the catalyst chamber, *C*. As it enters the chamber, it meets a stream of gaseous ammonia supplied from the container, *B*. The mixture of the two gases, air and ammonia, then passes over the catalyst contained in *C*, where oxidation of the ammonia takes place. The hot oxidation products resulting are cooled somewhat by passing them through a chamber (not shown in the figure) through which the air is passed in pipes before it enters the catalyst chamber. This serves the double purpose of preheating the air used and of cooling the oxidation products. The oxidation products then pass through the cooling chamber, *D*. Here a small percentage of nitric acid is formed by the interaction of the products of oxidation. Both the dilute nitric acid and the nitric oxide then enter the absorption tower, where the reaction continues, forming nitric acid containing about 60 per cent HNO_3. This can be further concentrated, if desired

about 60 per cent of HNO_3. This acid can be further concentrated, if desired, by adding sulfuric acid and distilling the mixture. This method, first devised in Germany, has been greatly improved in the United States, so that now all the nitric acid used for commercial purposes is prepared in this way.

Physical Properties · Pure hydrogen nitrate is a colorless liquid which has a density of 1.502 and boils at 86° with partial decomposition. At − 42° it freezes to a snowlike solid. An aqueous solution containing 68 per cent of hydrogen nitrate has a constant boiling point of 120.5° under a

pressure of 735 mm and distills with unchanged concentration. This solution has a density of 1.4 and constitutes the *concentrated nitric acid* of commerce.

Chemical Properties · Nitric acid is one of the strongest of acids, forming the ions H^+ and NO_3^- in aqueous solutions. Because of its unstable character and large percentage of oxygen, concentrated nitric acid acts as a strong oxidizing agent. Nitric acid readily decomposes into water, nitrogen dioxide, and oxygen, as represented in the following equation:

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

The nitrogen dioxide resulting from the decomposition is a reddish-brown gas which dissolves in the liquid, giving it a yellowish color. Nitric acid oxidizes charcoal to carbon dioxide, and sulfur to sulfuric acid. It readily reacts with many organic compounds, sometimes with explosive violence. Under carefully regulated conditions it forms compounds of the greatest commercial importance. Thus, with glycerin it forms *nitroglycerin*, which is the principal active constituent of dynamite; likewise with cellulose, the chief constituent of wood and cotton, it forms *nitrocellulose*, whose many commercial uses will be described in a later chapter.

Action of Nitric Acid on Metals · All the metals, with the exception of gold, platinum, and a few of the rare metals, are acted upon more or less readily by nitric acid. In discussing the action of nitric acid upon these metals it is convenient to divide them into two classes:

1. **Metals occurring above hydrogen in the electrochemical series.** At first thought it might be expected that hydrogen would be evolved (p. 233) when a dilute solution of nitric acid is acted upon by any of the metals occurring above hydrogen in the electrochemical series. It is evolved to a certain extent with a few of the metals, such as magnesium.

When one recalls, however, that nitric acid is a strong *oxidizing* agent, while hydrogen has strong *reducing* properties, it seems reasonable to suppose that nitric acid would be reduced by any hydrogen set free, yielding reduction products. Experiments show that this is what actually happens. The particular reduction products formed in any case depend upon the metal, the concentration of the acid, the temperature, and other conditions under which the reaction takes place. The following compounds represent successive steps in the reduction of nitric acid, with the corresponding changes in the oxidation state of nitrogen:

$$\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2} \longrightarrow \overset{+3}{HNO_2} \longrightarrow \overset{+2}{NO} \longrightarrow \overset{+1}{N_2O} \longrightarrow \overset{0}{N_2} \longrightarrow \overset{-1}{NH_2OH} \longrightarrow \overset{-3}{NH_3}$$

With 2 to 3 *M* nitric acid at 25°, powdered zinc gives ammonia:

$$4\ Zn + 10\ H^+ + NO_3^- \longrightarrow 4\ Zn^{++} + NH_4^+ + 3\ H_2O$$

However, with nitric acid stronger than $4M$, nitric oxide (NO) is the principal compound formed. The equation for the reaction is

$$3\ Zn + 8\ HNO_3 \longrightarrow 3\ Zn(NO_3)_2 + 2\ NO\uparrow + 4\ H_2O$$

2. Metals occurring below hydrogen in the electrochemical series. Those metals that occur below hydrogen in the electrochemical series, when acted upon by *dilute* nitric acid, usually yield nitric oxide. The general equation representing the reaction with copper, for example, is the following:

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

The equation may be broken down into two electronic partial equations:

Oxidation: $3 \times (Cu \longrightarrow Cu^{++} + 2\ e^-)$
Reduction: $2 \times (4\ H^+ + NO_3^- + 3\ e^- \longrightarrow NO\uparrow + 2\ H_2O)$

Since two electrons are lost in the first equation and three gained in the second, it is necessary to multiply the first by 3 and the second by 2 before adding to obtain the ionic equation

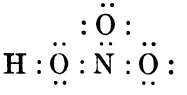
$$3\ Cu + 8\ H^+ + 2\ NO_3^- \longrightarrow 3\ Cu^{++} + 2\ NO\uparrow + 4\ H_2O$$

If *concentrated* acid is used instead of dilute, nitrogen dioxide is liberated rather than nitric oxide, as shown in the following equation:

$$Cu + 4\ HNO_3 \longrightarrow Cu(NO_3)_2 + 2\ NO_2\uparrow + 2\ H_2O$$

The Uses of Nitric Acid · The chief use of nitric acid is in the manufacture of nitroglycerin and nitrocellulose, widely utilized in the industrial world. It is also of great importance in the manufacture of fertilizers and dyes, and in addition has many minor uses.

Structural Formula of Hydrogen Nitrate · Since hydrogen nitrate is largely ionized in aqueous solution, it is evident that in dealing with such solutions we have to do not so much with the nitrate itself as with the ions which it forms, namely, H^+ and NO_3^-. The reactions of the pure compound, on the other hand, indicate that the atoms present in the molecule are combined as represented in the following structural formula:



Aqua Regia · In the writings of the alchemists frequent reference is made to *aqua regia* (royal water), so called because it readily dissolves gold ("the king of metals"), as well as all other metals. This liquid is formed by adding 1 part of nitric acid to from 2 to 4 parts of hydrochloric

acid. Though neither of these acids separately will dissolve gold or platinum, the mixture of the two readily does so. The strong solvent power of aqua regia is generally attributed to the liberation of chlorine in the nascent state, which converts the metals into chlorides, although with some metals further reactions take place, converting the resulting chlorides into more complex compounds. The final product formed when gold is dissolved in aqua regia is *chlorauric acid* ($HAuCl_4$).

There has been much discussion among chemists in regard to the nature of the reactions that take place when a metal dissolves in aqua regia, and even now the problem cannot be said to be solved. Since nitric acid is a strong oxidizing agent, one would naturally expect that this acid would oxidize the chlorine ions of the hydrochloric acid, as follows:

$$3\,HCl + HNO_3 \longrightarrow NO + 2\,H_2O + 3\,Cl$$

This equation, however, does not tell the whole story, since there is also formed a gaseous compound called nitrosyl chloride (NOCl), apparently by the combination of nitric oxide and nascent chlorine; this compound in turn may act as a catalyst. The final, complete reaction would then be

$$3\,HCl + HNO_3 \longrightarrow NOCl\uparrow + 2\,H_2O + 2\,Cl$$

Salts of Nitric Acid: the Nitrates · The salts of nitric acid are called *nitrates*. They can be obtained by the general method used for preparing salts, such as the action of nitric acid upon the metals themselves or upon their oxides or hydroxides. Some of these salts, especially sodium nitrate and potassium nitrate, are found in nature. The nitrates of most of the metals are white crystalline solids. The nitrate of copper is blue, that of nickel is green, while cobalt nitrate is cherry-red. All the normal nitrates are soluble in water and furnish the metallic ions and nitrate ions. Thus, potassium, calcium, and iron nitrates, already ionized in their crystals, yield their ions to the solution, as represented by the following equations:

$$K^+, NO_3^- \rightleftarrows K^+ + NO_3^-$$
$$Ca^{++}, 2\,NO_3^- \rightleftarrows Ca^{++} + 2\,NO_3^-$$
$$Fe^{+++}, 3\,NO_3^- \rightleftarrows Fe^{+++} + 3\,NO_3^-$$

When heated, the nitrates undergo decomposition. As a rule the metal is left in the form of its oxide, while oxygen and oxides of nitrogen are evolved. Thus, when copper nitrate is heated, the blue color of the nitrate gradually gives way to the black color of copper oxide, while the evolution of nitrogen dioxide is indicated by the reddish color of the evolved gas:

$$2\,Cu(NO_3)_2 \longrightarrow 2\,CuO + 4\,NO_2\uparrow + O_2\uparrow$$

In the case of a few nitrates, however, oxygen alone is evolved. Thus, sodium nitrate, when heated, forms sodium nitrite ($NaNO_2$) and oxygen:

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

The nitrates have various uses. Large quantities of sodium nitrate are exported from Chile to different countries, where it is used for the most part in fertilizers.

Nitrous Acid ***(HNO_2)*** · Sodium nitrite ($NaNO_2$), the sodium salt of nitrous acid, is readily formed by heating sodium nitrate with a mild reducing agent such as lead:

$$NaNO_3 + Pb \longrightarrow NaNO_2 + PbO$$

When this nitrite is treated with sulfuric acid, we should expect to have nitrous acid liberated (just as nitric acid is formed from a nitrate under similar conditions), according to the following equation:

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

If this reaction is carried out in very dilute solution, some nitrous acid is obtained; but the acid is so unstable that it soon decomposes, thus:

$$3\ HNO_2 \rightleftarrows HNO_3 + H_2O + 2\ NO\uparrow$$

In solutions at all concentrated the acid decomposes as fast as generated, forming water and oxides of nitrogen, as follows:

$$2\ HNO_2 \rightleftarrows H_2O + N_2O_3$$
$$N_2O_3 \rightleftarrows NO_2\uparrow + NO\uparrow$$

Nitrous acid may act as either an oxidizing agent or a reducing agent, depending on conditions. Thus, hydrogen iodide (a compound easily decomposed into hydrogen and iodine) is oxidized by the nitrous acid, as shown in the following equation:

$$2\ HI + 2\ HNO_2 \longrightarrow 2\ H_2O + 2\ NO + I_2$$

On the other hand, in the presence of a compound that readily gives up oxygen, nitrous acid combines with this oxygen, being changed thereby to nitric acid.

Hyponitrous Acid ***($H_2N_2O_2$)*** · When sodium nitrate is reduced under carefully regulated conditions, there is formed a compound, $Na_2N_2O_2$, called sodium hyponitrite. This is the sodium salt of *hyponitrous acid* ($H_2N_2O_2$). The free acid can be obtained from this salt in the form of colorless crystals, but it is very unstable and even likely to explode.

Hydroxylamine ***(H_2NOH)*** · This compound may be regarded as being composed of a hydroxyl group and an amino group, thus: NH_2–OH. It is intermediate between hydrogen peroxide (HO–OH) and hydrazine (H_2N–NH_2). Hydroxylamine was first obtained in dilute solution in 1865; but the compound was not isolated in a pure state until 1891, when De Bruyn obtained it in the form of

colorless needles melting at 34°. It is formed by the action of nascent hydrogen on nitric acid:

$$HNO_3 + 6\,H \longrightarrow NH_2OH + 2\,H_2O$$

It is often formed, therefore, when certain metals are dissolved in nitric acid.

Hydroxylamine resembles ammonia in being soluble in water and combining with it to form a base, $HO{-}NH_3^+$, OH^-. This base, however, is much less ionized and therefore weaker than ammonium hydroxide. By the action of strong acids the corresponding salts may be obtained. Thus, with hydrochloric acid there is formed the chloride, $HO{-}NH_3^+$, Cl^-. These salts are more stable than the free compound and are therefore more largely used.

Compounds of Nitrogen with Oxygen · The names, formulas, and physical states of the oxides of nitrogen are as follows:

Nitrous oxide (hyponitrous anhydride) (N_2O), a colorless gas.
Nitric oxide (NO), a colorless gas.
Nitrogen dioxide (NO_2), a gas, deep reddish brown in color.
Nitrogen trioxide (nitrous anhydride) (N_2O_3) exists only at low temperatures, both in liquid and in solid form.
Nitrogen pentoxide (nitric anhydride) (N_2O_5), a white crystalline solid.

Nitrous Oxide (Laughing Gas) (N_2O) · Nitrous oxide was first prepared by Priestley in 1772, two years previous to his discovery of oxygen. Davy determined its composition in 1800 and was the first to point out its physiological properties.

Preparation · Nitrous oxide can be prepared by the action of suitable reducing agents upon nitric acid, as well as upon nitric oxide. Priestley first obtained it from nitric oxide by the reducing action of iron:

$$2\,NO \longrightarrow N_2O + O$$

It is most conveniently prepared by heating ammonium nitrate. Just as ammonium nitrite, when heated, yields water and nitrogen (p. 106), so ammonium nitrate decomposes in a similar way, forming water and nitrous oxide. The similarity between the two reactions is shown in the following equations:

$$NH_4NO_2 \longrightarrow 2\,H_2O + N_2\uparrow$$
$$NH_4NO_3 \longrightarrow 2\,H_2O + N_2O\uparrow$$

Properties · Nitrous oxide is a colorless gas 1.53 times as heavy as air. It has a faint odor and its solution has a slightly sweetish taste. Liquid nitrous oxide is colorless and boils at $-89.5°$.

Chemically nitrous oxide is characterized by the ease with which it decomposes into free nitrogen and oxygen. It is therefore a good oxidizing agent. Such substances as carbon, iron, and phosphorus, when ignited and placed in jars of the gas, burn with brilliancy, forming oxides and

nitrogen. When inhaled it produces a kind of hysteria (whence the name *laughing gas*) and even unconsciousness and insensibility to pain. Davy (Fig. 15-2), who discovered this property of the gas, states that after breathing it he "danced about the laboratory as a madman." It has long been used as an anesthetic for minor surgical operations, such as those of dentistry, and is sold for this purpose, condensed in suitable containers.

***Nitric Oxide* (*NO*)** · Nitric oxide is formed at extremely high temperatures by direct reaction of nitrogen and oxygen. The reaction is reversible, and the nitric oxide formed at the high temperature will, if given time, decompose during cooling of the gas. However, the rate of decomposition decreases as the temperature decreases (p. 55), so that at temperatures below 1500° its rate of decomposition is negligible, and at room temperature nitric oxide is a stable gas. Hence it is possible to prepare nitric oxide by heating air (nitrogen plus oxygen) to a high temperature and cooling rapidly through the intermediate range before the nitric oxide has a chance to decompose. This is probably what happens in a lightning flash, and accounts for the oxides of nitrogen found after an electrical storm. A commercial process in which air was passed swiftly into and out of the hot zone around an electric arc was once used as a method of nitrogen fixation. Recently a method has been developed by which air is heated to 2100°, changing about 2% of the mixture to nitric oxide, and then cooled quickly by passing through a bed of magnesia pebbles.

In the laboratory, nitric oxide is readily prepared by the action of nitric acid (density 1.2) upon certain metals such as copper (p. 404).

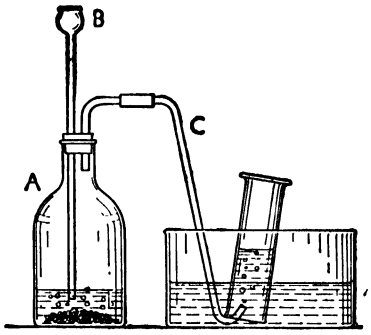


Fig. 23-5. Laboratory Preparation of Nitric Oxide

Laboratory preparation. The metal is placed in a flask, *A* (Fig. 23-5), and the acid slowly added through the funnel tube, *B*. After the air is driven out, the gas escapes through *C* and is collected over water. The gas at first evolved combines with the oxygen of the air contained in the flask to form the reddish-brown nitrogen dioxide, but this is absorbed as it bubbles through the water.

Properties · Nitric oxide is a colorless gas slightly heavier than air. It can be condensed to a liquid which boils at −151°. Nitric oxide is a much more stable compound than nitrous oxide; nevertheless it can be decomposed into its elements without difficulty. One of the most characteristic properties of nitric oxide is its conduct toward oxygen. When brought in contact with oxygen (or air), it forms nitrogen dioxide (NO_2).

***Nitrogen Dioxide* (NO_2)** · Nitrogen dioxide may be obtained by heating the nitrates of many of the heavier metals, such as lead nitrate or

copper nitrate, or by the direct union of nitric oxide and oxygen (Fig. 23-6). At ordinary temperatures it is a reddish-brown gas. When the gas is cooled the color fades, and a light-yellow liquid is obtained which boils at 21.3° and freezes to an almost colorless solid at − 9.3°.

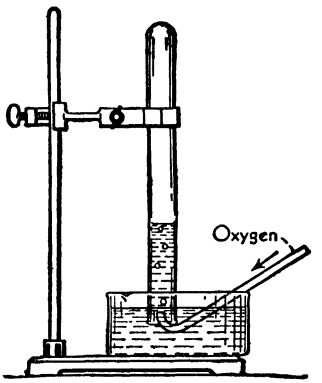


Fig. 23-6. The Formation of Nitrogen Dioxide

Nitrogen dioxide gives up half of its oxygen very easily, being converted into nitric oxide, and is a good oxidizing agent. It acts upon water in either of two ways, depending upon the temperature. In cold water both nitric and nitrous acids are formed:

$$2\ NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

At higher temperatures the nitrous acid decomposes as fast as formed, and the reaction may be represented as follows:

$$3\ NO_2 + H_2O \longrightarrow 2\ HNO_3 + NO\uparrow$$

Preparation of Nitrogen Dioxide · The formation of nitrogen dioxide from nitric oxide and oxygen, together with the reaction between the dioxide and water, may be shown as follows: A tube is filled with water and inverted in a vessel of water, as shown in Fig. 23-6. The tube is then nearly filled with nitric oxide, after which oxygen is admitted, a few bubbles at a time. As each bubble enters the tube, the deep reddish-brown dioxide forms. After a few moments the color fades, owing to the fact that the dioxide reacts with the water, which at the same time rises in the tube to take the place of the gas so removed.

Polymeric Compounds—Polymers · When the molecular weights of compounds are determined by measuring their vapor densities at temperatures not much above their boiling points, it is found that many of these vapors have molecular weights twice or more times as great as the simplest formula weight of the compound. At higher temperatures molecular weights corresponding to the simplest formula may be found. For example, the molecular weight of nitrogen dioxide at high temperatures corresponds to the formula NO_2, and the color of the gas is reddish brown; at lower temperatures the molecular weight is higher, nearly agreeing with formula N_2O_4, and the color is yellow. These facts indicate that there is an equilibrium between the two forms

$$N_2O_4 \rightleftarrows 2\ NO_2$$

and that the relative amounts of the two compounds change with temperature. A compound whose formula is a multiple of that of another compound is said to be a *polymer*, and the double compound nitrogen tetroxide, N_2O_4, is called a *dimer* of nitrogen dioxide.

Nitrogen Trioxide (N_2O_3) · When a mixture of equal volumes of nitric oxide and nitrogen dioxide is cooled, there is obtained at first a blue liquid, which, at a still lower temperature, freezes to a solid. The liquid, as well as the solid, is generally regarded as nitrogen trioxide:

$$NO + NO_2 \longrightarrow N_2O_3$$

Nitrogen Pentoxide (N_2O_5) · This oxide is a white crystalline unstable solid and is formed when nitric acid is treated with a strong dehydrating agent, such as phosphorus pentoxide:

$$2\ HNO_3 \longrightarrow H_2O + N_2O_5$$

The Fixation of Nitrogen by Plants · Our bodies must depend for life on compounds of nitrogen, but are not able to assimilate directly the free nitrogen in the atmosphere. They obtain their supply in the form of compounds of nitrogen (*proteins*) present in such foods as milk, eggs, meat, beans, and peas. Plants do somewhat better, for some of them are able, by indirect means, to utilize free nitrogen.

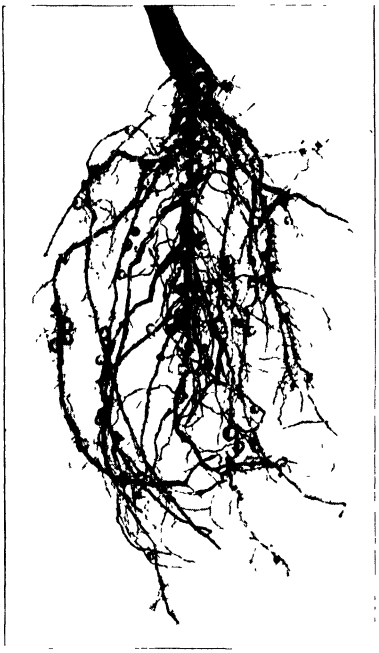


Fig. 23-7. Nodules on the Roots of a Soybean Plant

It has long been known that a few plants, and especially those belonging to the *legume* family, such as beans, clover, alfalfa, and peas, not only thrive in poor soil but enrich the soil in which they grow. These plants are able to do this because of the presence in the soil of certain *nitrogen-fixing* bacteria (genus *Rhizobium*). When a legume begins to grow in a soil which contains these bacteria, the bacteria will enter the root cells and multiply with great rapidity, forming the well-known nodules on the roots of legumes (Fig. 23-7). These bacteria are parasitic and obtain their food from the plant, assimilating a part of it into their own tissues and oxidizing a part of it. They utilize the energy thus available in building up nitrates from the free nitrogen absorbed by the soil from the atmosphere. The nitrates are assimilated by the plant and converted to plant protein. It is a sort of co-operative enterprise, in which the legume furnishes the home and food for the bacteria, and the bacteria in turn furnish the plant with one of its essential foods.

Until recently only a few kinds of microorganisms were thought to fix the nitrogen of the atmosphere in the form essential to higher plant and animal life. Now a number of others have been found. Possibly the organisms in the sea, including blue-green algae, fix even more nitrogen than do those in the world's soil.

The Nitrogen Cycle · When an animal eats plant protein this protein is changed by digestion into nitrogen compounds called *amino acids*, which are rebuilt into animal protein tissues. These in turn are eventually converted, by body processes, into such animal waste products as urea and ammonia.

In addition to the nitrogen-fixing bacteria, the soil contains other kinds of bacteria. One kind, the *nitrifying bacteria*, decompose nitrogenous organic matter (such as animal wastes, and plants which have been plowed

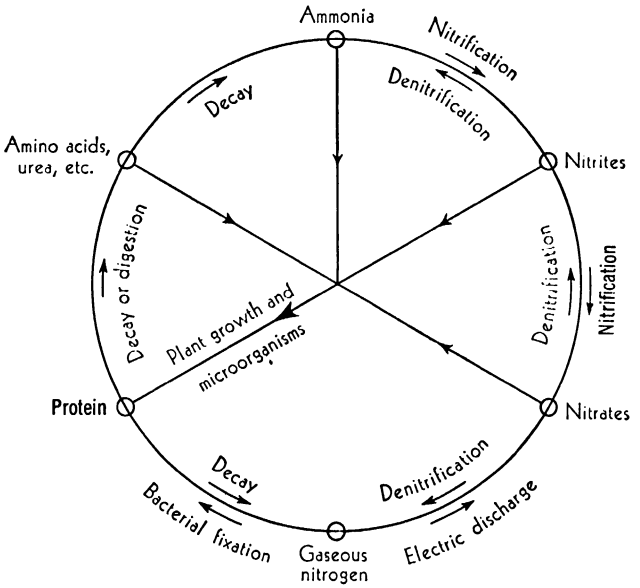


Fig. 23-8. The Nitrogen Cycle · Courtesy of the *Journal of Chemical Education*

under). The nitrogen is changed first into nitrites and then into nitrates. Thus organic nitrogen is made available in a form that is usable by plants. Soils that are not well aerated may contain yet a third kind of organism, known as *denitrifying bacteria*, which have an effect opposite to that of the nitrifying bacteria, reducing any nitrates present into nitrites and free nitrogen (and even ammonia). While some nitrogen is thus set free (if denitrifying bacteria are present), this is offset by the fixation of

nitrogen in usable form by the nitrogen-fixing bacteria, as well as by electric discharges during thunderstorms.

The various changes in which the nitrogen atom participates are referred to by Mellor in the following imaginative way: "Today a nitrogen atom may be throbbing in the cells of the meadow grass; tomorrow, it may be pulsating through the tissues of a living animal. The nitrogen atom afterward may rise from decaying animal refuse, and stream to the upper regions of the atmosphere, where it may be yoked with oxygen in a flash of lightning and return as plant food to the soil in a torrent of rain; or it may be directly absorbed from the atmosphere by the soil, and there rendered available for plant food by the action of bacteria. Thus each nitrogen atom has doubtless undergone a never-ceasing cycle of changes through countless aeons of time."

There are about seventy-five thunderstorms in progress at different places on the earth's surface all the time; and the oxides of nitrogen, formed in the path of the lightning bolts, are carried by falling raindrops into the soil. Tests conducted over a series of years in typical localities show that the fixed nitrogen added in this way amounts to about 7 lb annually per acre of ground. Finally, in districts given up to agriculture large amounts of manufactured nitrogen compounds are applied to the soil as *fertilizers*, usually as sodium nitrate or ammonium sulfate or urea (made commercially from ammonia and carbon dioxide).

United States Production of Nitrogen Compounds · The maximum annual consumption of nitrogen compounds in the United States before 1941 was approximately 540,000 short tons of fixed nitrogen, about 83 per cent of which went into fertilizers. The postwar reconversion period found the United States with the tremendous production capacity of 1,500,000 to 1,700,000 short tons. The consumption is now more than 1,500,000 tons—a large part of it for agricultural purposes.

Phosphorus

History · The element phosphorus was discovered by the alchemist Brand, of Hamburg, in 1669, while he was searching for the philosophers' stone. Owing to its peculiar properties and the secrecy which was maintained about its preparation, it remained a very rare and costly substance until the demand for it in the manufacture of matches brought about its production on a large scale. There are two fundamental allotropic forms of phosphorus, *white* (sometimes called *yellow*) *phosphorus* and *violet*, or *metallic, phosphorus*. Between these is a partially changed variety called *red phosphorus*.

White Phosphorus · The usual form of phosphorus, white (or yellow) phosphorus, is really a colorless, translucent, waxy solid, which melts at

44.1°, boils at 280°, and has a density of 1.82 at ordinary temperatures. It is sold in the form of candle-like sticks, and is insoluble in water but dissolves in carbon disulfide and turpentine. It is an extremely active substance, combining directly with most of the elements, especially with oxygen. When but slightly warmed, it burns with a sputtering flame, evolving white clouds of the oxides P_4O_6 and P_4O_{10}. Because of its low kindling temperature (about 30°), it is always preserved and handled under water. It is a violent poison. Below 400° phosphorus vapor has the formula P_4.

The Slow Oxidation of Phosphorus · There are many peculiarities attending the slow oxidation of phosphorus. A stick lying half covered with water is slowly oxidized, and ozone is formed at the same time. Of the total oxygen used up, half goes to oxidize the phosphorus and half to combine with molecular oxygen to form ozone. The energy absorbed in the formation of the latter is furnished by the oxidation of the phosphorus. In the slow oxidation of phosphorus, light (which can be seen in a dark room) is given off, though the temperature is below the kindling temperature. This striking phenomenon suggested the name *phosphorus* ("light-bearer"); and although other materials act in a similar way, the phenomenon is called *phosphorescence.*

Red Phosphorus · When white phosphorus is heated out of contact with oxygen, it is converted into a different substance, called red phosphorus. This change goes on very slowly at ordinary temperatures, is very marked at about 250°, and at 300° is fairly rapid. It can be hastened by catalysts, especially by iodine or selenium. Under ordinary conditions the transition into violet phosphorus is never complete; so red phosphorus is a partially changed form and varies considerably in its properties. The pure violet form can be obtained by crystallization of phosphorus from lead.

If the red phosphorus is vaporized, it gives a vapor which is identical with that from the white form; and on condensation the latter variety is always obtained. This is in accordance with the general rule that *when a substance capable of existing in several forms is condensed from the gaseous state or crystallized from the liquid state, the least stable variety forms first, and this, on standing, passes into the more stable form.*

Red phosphorus is not soluble in carbon disulfide, is not poisonous, and has a smaller heat of combustion than the white form. It does not combine with oxygen at ordinary temperatures and must be heated to about 260° before ignition takes place.

Occurrence · Owing to its great chemical activity, phosphorus never occurs free in nature. In the form of phosphates it is very abundant and

widely distributed. *Phosphorite* ($Ca_3(PO_4)_2$) is the chief mineral form of calcium phosphate, while *apatite* consists of calcium phosphate combined with calcium fluoride or calcium chloride. In the form of *phosphate rock* these minerals, mixed with many impurities, are found in large quantities in the United States, especially in Florida, Tennessee, Idaho, and Montana, and are mined in enormous quantities (about 9,000,000 tons annually), largely for use in the manufacture of fertilizers. Many other countries produce phosphates, especially Morocco and Tunisia. Calcium phosphate is a constituent of all fertile soil. It is the chief mineral constituent of the bones of animals, and bone ash is therefore principally calcium phosphate. Phosphorus is also present in brain and nerve tissues and in various secretions, so that there is a total of about 1 per cent of this element in the human body.

Preparation · At present phosphorus is usually prepared by heating mineral phosphates or bone ash with coke and sand (chiefly silica, SiO_2) in a specially constructed electric furnace, the main features of which are shown in Fig. 23-9. At the temperature employed silica is not volatile, while phosphoric anhydride (P_4O_{10}) is; consequently the volatile anhydride is displaced:

$$\underset{\text{calcium phosphate}}{2\,Ca_3(PO_4)_2} + \underset{\text{silica}}{6\,SiO_2} \longrightarrow \underset{\text{calcium silicate}}{6\,CaSiO_3} + \underset{\text{phosphoric anhydride}}{P_4O_{10}}$$

The carbon present then reduces the oxide of phosphorus:

$$P_4O_{10} + 10\,C \longrightarrow 10\,CO\uparrow + P_4\uparrow$$

The charge of phosphate, coke, and sand is fed into the furnace from the hopper, *A* (Fig. 23-9), by the worm screw, *B*, while the liquid calcium silicate is drawn off at *C* as a slag or glass. The vapors of phosphorus escape at *D*, together with the carbon monoxide, and are condensed to a liquid by a suitable water condenser. The liquid is purified by filtration through chamois skin or porous stone, and is finally run into molds immersed in cold water, and hardened into sticks for the market. Low-grade phosphate rock can be used in this process.

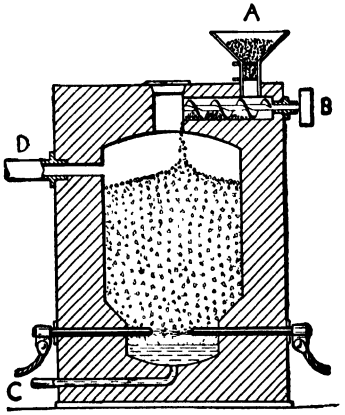


Fig. 23-9. Furnace for the Production of Phosphorus

Uses of Phosphorus · The largest use of free phosphorus is in the manufacture of certain bronzes. A large percentage is burned to P_4O_{10}, which is then converted to phosphoric acid, and a further large amount is used to make the sulfide P_4S_3

for the manufacture of matches. During war large amounts are used in generating smoke clouds, since phosphorus burns readily and forms a dense white smoke of oxides of phosphorus, which serves to conceal troops and ships. It is used also in tracer bullets. An important use of red phosphorus is in the *manufacture of matches.*

Matches · It has been said that the greatest discovery ever made was that of fire. Certainly one of the most useful, if not the greatest, of inventions was that of starting a fire by the use of matches. Friction matches containing phosphorus were first introduced by Walker of England about 1826. At present two general varieties are in common use, namely, the "strike-anywhere" and the safety match. In the former the materials used are (1) an oxidizing agent (potassium chlorate); (2) an oxidizable substance, such as paraffin or sulfur; (3) a binding material (glue); (4) a filling material, such as ground glass. The *tip* of the match contains, in addition to the materials mentioned above, a large percentage of phosphorus sesquisulfide (P_4S_3). By friction the phosphorus sesquisulfide ignites, and the combustion is supported by the oxidizing agent and communicated to the wood by the slowly burning paraffin. A number of other substances (starch, clay, plaster of Paris) are often used to impart desirable properties, such as resistance to moisture and regulation of speed of combustion.

In the Swedish, or safety, match, red phosphorus, an oxidizing agent, and some gritty material, such as powdered glass, are mixed with glue and placed on the side of the box. The match tip is provided with an oxidizing agent and an easily combustible substance, usually antimony sulfide. The match cannot be ignited easily by friction except on the prepared surface of the box.

Constant working with white phosphorus frequently results in dreadful diseases of the bones of the face, while many disastrous fires are caused by accidental ignition of matches containing it. On both accounts the manufacture and use of matches containing white phosphorus is prohibited by law in all civilized countries.

Hydrides of Phosphorus—Phosphine (PH_3) · Phosphorus forms several compounds with hydrogen, the best known of which is *phosphine* (PH_3), the analogue of ammonia (NH_3).

Phosphine is a gas of unpleasant odor and is exceedingly poisonous. Like ammonia, it forms salts with the halogen acids. Thus, we have *phosphonium chloride* (PH_4Cl) and *phosphonium iodide* (PH_4I), analogous to ammonium chloride and ammonium iodide.

Preparation of Phosphine · The simplest way of making phosphine is to treat calcium phosphide with water:

$$Ca_3P_2 + 6\ H_2O \longrightarrow 3\ Ca(OH)_2 + 2\ PH_3\uparrow$$

It is more conveniently made by boiling white phosphorus suspended in

a concentrated solution of sodium hydroxide. The reaction must be carried out in the absence of air.

$$P_4 + 3\ NaOH + 3\ H_2O \longrightarrow 3\ NaH_2PO_2 + PH_3\uparrow$$

Halogen Compounds of Phosphorus · Phosphorus forms at least two compounds with each of the halogen elements, usually of the formulas PX_3 and PX_5. Of these, the chlorides are the most important, especially in the preparation of organic compounds. They are formed by the direct combination of phosphorus with chlorine.

1. **Phosphorus trichloride.** This is a colorless liquid which fumes strongly in moist air, owing to the formation of *phosphorous acid*:

$$PCl_3 + 3\ H_2O \longrightarrow 3\ HCl + H_3PO_3$$

2. **Phosphorus pentachloride.** This is a nearly white solid which, like the trichloride, acts on water, forming *phosphoric acid*:

$$PCl_5 + 4H_2O \longrightarrow 5HCl + H_3PO_4$$

When heated, the pentachloride dissociates into the trichloride and free chlorine, which recombine on cooling:

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

Oxides of Phosphorus · Two common oxides of phosphorus are known. (1) The formula for the molecule of *phosphorous anhydride*, or *phosphorus trioxide*, was formerly thought to be P_2O_3 but is now known to be P_4O_6. (2) *Phosphoric anhydride*, or *phosphorus pentoxide*, is P_4O_{10} (Fig. 23-10). They are both white, snowlike solids. When phosphorus burns in *excess* oxygen or air, the pentoxide is formed; if the supply of oxygen is limited, a mixture of the two oxides results. The pentoxide is an exceedingly stable compound and has neither oxidizing nor reducing properties. It combines with water with such energy that it will thoroughly dry a moist gas passed over it. The trioxide takes up oxygen with great ease and is a strong reducing agent. Heated above 400°, it decomposes into phosphorus and phosphorus tetroxide (P_2O_4).

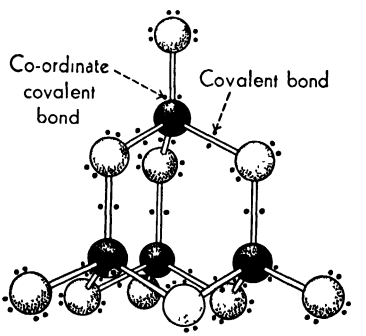


Fig. 23-10. Model of a Molecule of P_4O_{10}. The darker balls represent atoms of phosphorus

Acids of Phosphorus · Both the trioxide and the pentoxide are typical acid anhydrides (p. 283). They combine with water directly, and the

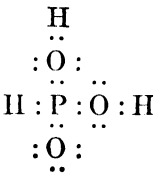
final products of the reaction are respectively *phosphorous* acid (H_3PO_3) and *phosphoric* acid (H_3PO_4):

$$P_4O_6 + 6\ H_2O \longrightarrow 4\ H_3PO_3 \quad (1)$$
$$P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4 \quad (2)$$

By control of temperature and the proportion of water still other acids can be obtained from these oxides, differing from one another in the ratio between the oxide and the water. Their names, formulas, and relations are shown in the following table:

ACIDS OF PHOSPHORUS	
PHOSPHOROUS ACIDS	PHOSPHORIC ACIDS
Ortho- . . $P_4O_6 + 6\ H_2O \longrightarrow 4\ H_3PO_3$	Ortho- . $P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4$
Pyro- . . $P_4O_6 + 4\ H_2O \longrightarrow 2\ H_4P_2O_5$	Pyro- . . $P_4O_{10} + 4\ H_2O \longrightarrow 2\ H_4P_2O_7$
Meta- . . $P_4O_6 + 2\ H_2O \longrightarrow 4\ HPO_2$	Meta- . . $P_4O_{10} + 2\ H_2O \longrightarrow 4\ HPO_3$

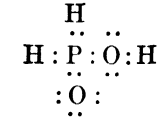
The Phosphorous Acids · The only one of the phosphorous acids at all well known is orthophosphorous acid (H_3PO_3), commonly called simply *phosphorous acid.* It may be prepared by the action of phosphorus trihalides on water (pp. 272, 416). The pure compound forms transparent crystals. It is generally regarded as a *dibasic* acid (H_2HPO_3), although the salt Na_3PO_3 has been described. Like the trioxide from which it is derived, it is a strong reducing agent. When heated, three molecules are oxidized to phosphoric acid by the oxygen given up by a fourth molecule, thus:



$$3\ H_3PO_3 + H_3PO_3 \longrightarrow 3\ H_3PO_4 + PH_3\uparrow$$

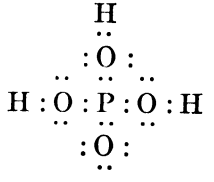
A reaction of this kind is called *autoxidation-reduction.*

Hypophosphorus Acid (H_3PO_2) · This acid can be prepared from the salt NaH_2PO_2, obtained in the preparation of phosphine (p. 415). It is a *monobasic* acid (HH_2PO_2). Its salts, the *hypophosphites*, find frequent applications in medicine.



The Phosphoric Acids · Since all three of the phosphoric acids are derived from the stable pentoxide, it is not surprising that, like it, they should have neither oxidizing nor reducing properties.

Orthophosphoric Acid ***(H_3PO_4)*** · This acid is the form into which all other acids of phosphorus tend to pass when in solution, either by hydration or by oxidation. The anhydrous compound,



properly called *hydrogen phosphate,* is sometimes prepared by burning white phosphorus in air and completing the oxidation with nitric acid. At present increasing amounts of the acid are prepared by burning in air the vapor of phosphorus liberated in the preparation of the element (Fig. 23-9) and combining the resulting oxide with water. The compound forms colorless hydrated crystals, which melt at 42.3°. For commercial purposes the acid has usually been prepared by treating calcium phosphate with concentrated sulfuric acid and filtering off the nearly insoluble calcium sulfate:

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \longrightarrow 2\ H_3PO_4 + 3\ CaSO_4\downarrow$$

In solution, hydrogen phosphate acts as a *tribasic* acid. It is therefore capable of forming three series of salts, according as one, two, or three hydrogen atoms are replaced by metals. The formulas and the method of naming such salts are illustrated in the following table of the three sodium salts:

SODIUM SALTS OF ORTHOPHOSPHORIC ACID	
FORMULA	NAME
Na_3PO_4	Trisodium phosphate; normal, or tertiary, sodium phosphate
Na_2HPO_4	Disodium phosphate; secondary sodium phosphate
NaH_2PO_4	Monosodium phosphate; primary sodium phosphate

The heavy metals, such as silver or mercury, form only the normal, or tertiary, phosphates. Salts are also known in which there is more than one kind of cation. The most familiar ones are *microcosmic salt* ($NaNH_4HPO_4 \cdot 4\ H_2O$) and *magnesium ammonium phosphate* ($MgNH_4PO_4$).

The normal salts of the alkáli metals sodium and potassium are very strongly hydrolyzed in solution (p. 451):

$$3\ Na^+,\ PO_4^{---} + H_2O \rightleftarrows 2\ Na^+,\ HPO_4^{--} + Na^+,\ OH^-$$

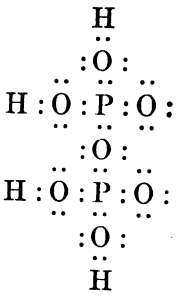
Because of the alkaline character of solutions of trisodium phosphate, this salt has a wide use for cleansing purposes and for softening hard water. The normal calcium phosphate ($Ca_3(PO_4)_2$) is only very slightly soluble. When treated with sulfuric acid it is changed into the more soluble primary salt, thus:

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\ CaSO_4$$

Advantage is taken of this reaction in the manufacture of fertilizers, so as to obtain the phosphorus in a more soluble or available form. The calcium sulfate formed seems also to add to the value of the fertilizer. Nearly one third of the total production of sulfuric acid is used for this purpose. The mixture of soluble acid phosphate and calcium sulfate formed when rock phosphate is treated in this way is called *superphosphate.*

Pyrophosphoric Acid **($H_4P_2O_7$)** · On heating phosphoric acid to about 225°, pyrophosphoric acid is formed, in accordance with the following equation:

$$2\ H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O\uparrow$$



It is a white crystalline solid. Its salts can be prepared by heating a monohydrogen phosphate:

$$2\ Na_2HPO_4 \longrightarrow Na_4P_2O_7 + H_2O\uparrow$$

Acids such as pyrophosphoric acid, formed by the union of two or more molecules of the simpler acid, through loss of water, are called *condensed acids.*

Metaphosphoric Acid **(*Glacial Phosphoric Acid*) (HPO_3)** · This acid is formed when phosphoric acid is heated above 400°:

$$H_3PO_4 \longrightarrow HPO_3 + H_2O\uparrow$$

It is also formed when phosphoric pentoxide is treated with *cold* water:

$$P_4O_{10} + 2\ H_2O \longrightarrow 4\ HPO_3$$

Its salts are readily obtained by heating a dihydrogen phosphate:

$$NaH_2PO_4 \longrightarrow NaPO_3 + H_2O\uparrow$$

It is a white crystalline solid and is so stable toward heat that it can be fused and even volatilized without decomposition. On cooling from the fused state it forms a glassy solid, and on this account is often called *glacial* phosphoric acid. It possesses the property of dissolving small quantities of metallic oxides, with the formation of compounds which, in the case of certain metals, have characteristic colors. It is therefore used in chemical analysis for the detection of these metals.

There is considerable evidence that fused sodium metaphosphate exists as a complex compound whose general formula is $Na_6P_6O_{18}$ (sodium hexametaphosphate). This ionizes only partly, thus:

$$Na_6P_6O_{18} \longrightarrow 2\ Na^+ + Na_4P_6O_{18}^{--}$$

This salt may be used to soften water, since it has the property of reacting with calcium or magnesium ions in such a way as to include

them in the complex ion, thus removing them from water in which they are found:

$$Na_4P_6O_{18}^{--} + 2\,Ca^{++} \longrightarrow 4\,Na^{+} + Ca_2P_6O_{18}^{--}$$

Sulfides of Phosphorus · A number of compounds consisting of phosphorus and sulfur can be obtained by heating the two elements in various proportions. The most important of these has the formula P_4S_3, and is called *phosphorus sesquisulfide.* As we have seen, it is an important component in the manufacture of matches.

Arsenic

History and Occurrence · Compounds of arsenic have been known from the earliest times. The highly colored sulfides *realgar* (As_2S_2) and *orpiment* (As_2S_3) are found in nature, and have been used as pigments since the time of Aristotle. *Arsenopyrite* (FeAsS), or *mispickel*, is an abundant mineral, and the corresponding *cobaltite* (CoAsS) is not rare. The element is occasionally found in the free form, and also as the oxide As_4O_6, called *arsenolite.* It is very widely distributed in small percentages in the sulfide ores of many metals, and these metals, as well as products prepared from the sulfur of their ores, are apt to be contaminated with arsenic. Practically all the arsenic used in the United States is obtained in the form of the trioxide, As_4O_6, as a by-product in the smelting of ores of copper and lead.

Preparation and Properties · The element is prepared by subliming the natural product or by heating arsenopyrite:

$$4\,FeAsS \longrightarrow 4\,FeS + As_4\uparrow$$

It is prepared in pure form by reducing the oxide with carbon. Like phosphorus, it occurs in several allotropic forms, the most important of which is the so-called gray, or metallic, arsenic. This is obtained as a gray crystalline mass, somewhat resembling coke in appearance, by slowly cooling the vapor of arsenic. If arsenic is heated, its vapor pressure increases rapidly and reaches 760 mm at a temperature much below its melting point; consequently it sublimes without melting. All forms give the same yellowish vapor, the density of which corresponds to the molecular formula As_4. Heated in air, arsenic forms the oxide As_4O_6. It combines with chlorine to form the trichloride, $AsCl_3$. It also combines with many of the metals, and the resulting compounds are called *arsenides.*

The element readily alloys with some of the metals, and its alloy with lead is used for making shot. The alloy is harder than pure lead, and

the shot made from it is more nearly spherical. The chief use of arsenic is in the manufacture of its compounds.

***Arsine* (AsH_3)** · When hydrogen is generated in contact with compounds of arsenic, *arsine* (AsH_3) is formed. The reaction when oxide of arsenic is so treated is

$$As_4O_6 + 24\ H \longrightarrow 6\ H_2O + 4\ AsH_3\uparrow$$

Arsine is a gas with a peculiar, garlic-like odor and is intensely poisonous. A single bubble of the pure gas has been known to prove fatal. It is an unstable compound, decomposing into its elements when heated to a moderate temperature:

$$4\ AsH_3 \longrightarrow As_4 + 6\ H_2$$

It is combustible and burns with a pale, bluish-white flame to form arsenic trioxide and water when air is in excess:

$$4\ AsH_3 + 6\ O_2 \longrightarrow As_4O_6 + 6\ H_2O$$

When the supply of air is deficient, water and metallic arsenic are formed:

$$4\ AsH_3 + 3\ O_2 \longrightarrow 6\ H_2O + As_4$$

These reactions make the detection of even minute quantities of arsenic an easy problem.

Marsh's Test for Arsenic · Marsh's method for detecting arsenic illustrates the formation and properties of arsine. Hydrogen is generated in the flask, *A* (Fig. 23-11), by the action of dilute sulfuric acid on zinc, is dried by being passed over calcium chloride in the tube *B*, and, after passing through the hard-glass tube, *C*, is ignited at the jet, *D*. If a substance containing arsenic is now introduced into the generator, *A*, the arsenic is converted into arsine by the action of nascent hydrogen and passes to the jet, along with excess hydrogen. If the tube *C* is strongly heated at some point near the middle, the arsine is decomposed while passing this point, and the arsenic is deposited just beyond the heated point in the form of a shining, brownish-black mirror. A small fraction of a milligram of arsenic can be detected by this test. If the tube is not heated, the arsine burns, along with the hydrogen, at the jet. Under these conditions a small porcelain dish crowded down into the flame is blackened by a spot of metallic

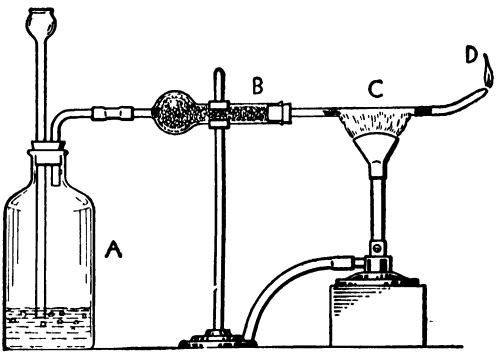


Fig. 23-11. Marsh's Apparatus for the Detection of Arsenic

arsenic; for the arsine is decomposed by the heat of the flame, and the arsenic, cooled below its kindling temperature by the cold porcelain, deposits upon it as a black spot. Antimony gives a similar deposit, but it is easy to distinguish between the two.

Halogen Compounds · With all four halogen elements arsenic forms low-melting, low-boiling trihalides, the best-known of which is the chloride, $AsCl_3$. The pentafluoride, AsF_5, is also known. These halides are hydrolyzed by water, but not so readily as are the corresponding phosphorus compounds.

Oxides of Arsenic · There are two well-known oxides of arsenic, namely, (1) *arsenious oxide* (As_4O_6), or *arsenic trioxide*, and (2) *arsenic oxide* (As_4O_{10}), also called *arsenic pentoxide*. Both are acid anhydrides.

1. **Arsenious oxide (arsenic trioxide).** This is the best-known compound of arsenic and is often called *white arsenic* or simply *arsenic*. In the vapor state, as well as in the crystalline solid, its molecule has the formula As_4O_6 (Fig. 23-12). When metallic ores containing arsenic are smelted, the arsenic is converted into the oxide, which condenses in the flues as a fine dust, from which the pure oxide may be obtained by sublimation, as it is readily volatile. The copper and lead smelters of Montana, Nevada, Utah, and Texas are the chief source of arsenic in the United States. Canada also produces much arsenious oxide from similar sources.

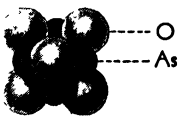


Fig. 23-12. The As_4O_6 Molecule

Arsenious oxide can be obtained in at least three allotropic forms. One of these is amorphous and in appearance resembles lumps of porcelain. The other two are crystalline, the more stable one being octahedral, the other rhombic. The oxide is only slightly soluble in water (the amorphous form much more so than the octahedral). It has a sweetish taste and is *extremely poisonous*, but one can acquire a tolerance for it through gradually increased doses. In some countries the mountaineers say that it increases their endurance in mountain-climbing, and they gradually become accustomed to daily portions much larger than a fatal dose for an ordinary person.

Arsenious oxide is the compound from which all other arsenic compounds are prepared. Its greatest use is in the preparation of insecticides; to some extent it is used to decolorize glass. A number of complex compounds of arsenic are used in medicine, the best-known of which is *salvarsan*.

2. **Arsenic pentoxide.** This is a white amorphous solid whose formula is As_4O_{10} (analogous to P_4O_{10}, Fig. 23-10). When heated, it decomposes into the trioxide and oxygen.

Acids of Arsenic · Arsenic forms two series of oxygen acids, derived from the two oxides, analogous to those of phosphorus. The names and formulas of these are as follows:

ACIDS OF ARSENIC			
ARSENIOUS ACIDS		ARSENIC ACIDS	
Orthoarsenious acid	H_3AsO_3	Orthoarsenic acid	H_3AsO_4
Pyroarsenious acid	$H_4As_2O_5$	Pyroarsenic acid	$H_4As_2O_7$
Metarsenious acid	$HAsO_2$	Metarsenic acid	$HAsO_3$

The Arsenious Acids · When dissolved in water, arsenic trioxide gives rise to a number of different acids, none of which has been obtained in pure condition and all of which are very weak. By suitable means the salts of these acids can be obtained; those of sodium and potassium are derived from the metarsenious acid, $HAsO_2$, while those of most of the other metals are derived from the ortho acid, H_3AsO_3. Thus, the potassium salt is $KAsO_2$, while the silver salt is Ag_3AsO_3. Salts of the pyro acid, $H_4As_2O_5$, are also known. The copper salts are of importance. *Scheele's green* ($CuHAsO_3$) is used as a pigment. *Paris green* is used as a poison for insects. It is generally given the formula $(Cu(AsO_2)_2)_3 \cdot Cu(C_2H_3O_2)_2$, in accordance with which it must be regarded as a combination of copper metarsenite and copper acetate. Combinations of two salts are called *double salts*. Freshly precipitated ferric hydroxide adsorbs arsenic compounds and serves as an antidote for arsenic poisoning. Arsenious acid may be oxidized to arsenic acid, but a strong oxidizing agent must be used.

The Arsenic Acids · When arsenic trioxide is boiled with nitric acid and the solution is evaporated to a sirup, crystals of orthoarsenic acid ($2\,H_3AsO_4 \cdot H_2O$) are obtained. Salts of this acid are not infrequently found in nature, and many have been prepared in the laboratory. Calcium arsenate ($Ca_3(AsO_4)_2$) and lead arsenate are widely used insecticides. The reddish-brown silver salt (Ag_3AsO_4) and the magnesium ammonium salt ($MgNH_4AsO_4$) are of importance in analytical chemistry. All these salts are quite similar to the corresponding phosphates. Unlike phosphoric acid, arsenic acid is an oxidizing agent, as might be anticipated from the instability of its anhydride.

Sulfides of Arsenic · There are three well-known sulfides of arsenic, namely, As_2S_2, As_2S_3, and As_2S_5.

1. **Arsenic disulfide (realgar) (As_2S_2).** Realgar is a brittle, red solid and can be prepared by heating arsenic and sulfur together in the proper proportions.

2. **Arsenic trisulfide (orpiment) (As_2S_3).** This sulfide, a yellow, crystalline solid, is formed when hydrogen sulfide is passed into an acidified solution of arsenic trioxide:

$$As_4O_6 + 6\ H_2S \longrightarrow 2\ As_2S_3\downarrow + 6\ H_2O$$

3. **Arsenic pentasulfide (As_2S_5).** This compound, along with arsenic trisulfide, forms as a yellow precipitate when hydrogen sulfide is passed into a solution of arsenic acid to which hydrochloric acid has been added:

$$2\ H_3AsO_4 + 5\ H_2S \longrightarrow As_2S_5\downarrow + 8\ H_2O$$

Thio Salts of Arsenic · When either the trisulfide or the pentasulfide is treated with a solution of a *soluble sulfide*, such as sodium sulfide (Na_2S) or ammonium sulfide ($(NH_4)_2S$), it is dissolved; and when the solution is evaporated, well-crystallized *thio salts* are obtained:

$$As_2S_3 + 3\ Na_2S \longrightarrow 2\ Na_3AsS_3$$
$$As_2S_5 + 3\ Na_2S \longrightarrow 2\ Na_3AsS_4$$

These salts may be regarded as derived from the corresponding oxygen salts by the replacement of oxygen with sulfur. Thio salts corresponding to both the pyro and the meta acids are also known. All these salts are easier to obtain in well-crystallized form than the oxygen salts. On treatment with acids they are decomposed, with the formation of sulfides:

$$2\ Na_3AsS_4 + 6\ HCl \longrightarrow 6\ NaCl + As_2S_5\downarrow + 3\ H_2S\uparrow$$

In chemical analysis these reactions make it possible to separate the sulfides of arsenic from those of other elements which are insoluble in sodium or ammonium sulfides.

Antimony

Historical · Compounds of antimony, as well as the element itself, have been known from the earliest times. The Chaldeans appear to have made ornamental vessels of the metal. The Chinese employed preparations of antimony as drugs. The sulfide Sb_2S_3, known as *stibnite*, was called *stibium* by Pliny; and the name *antimonium* first appears in the works of the alchemist Geber. In the fifteenth century, compounds of antimony were widely used as medicines.

Occurrence and Uses · The chief ore of antimony is stibnite. This is rather widely distributed in different countries, but the supply comes principally from China, Mexico, Czechoslovakia, and Bolivia. The United States produces a small amount only.

Antimony is rarely used in the pure state, but is melted with other low-melting metals (for example, lead) to form alloys, such as type metal,

Babbitt metal, and pewter. The metal may be obtained by reducing the oxide Sb_2O_3 with carbon or the sulfide with iron:

$$3\ Fe + Sb_2S_3 \longrightarrow 3\ FeS + 2\ Sb$$

Physical Properties · Like phosphorus and arsenic, antimony exists in several distinct forms, the familiar one being the ordinary gray form. The latter is a silvery, shining metal, very brittle, forming crystals which, like those of gray arsenic, belong to the hexagonal system. Its density is 6.68, and its melting point 630.5°. Some of its alloys expand on solidification. Its boiling point is 1380°; and its vapor consists of the molecules Sb_2 and Sb_4.

Chemical Properties · In its compounds antimony may be either pentavalent, tetravalent, or trivalent. In the compounds in which it is trivalent it plays the part of a metal; as a pentavalent element it is, like arsenic, a nonmetal. *It stands midway between arsenic, which is strictly acid-forming, and bismuth, which is base-forming.* Antimony is not attacked by dilute acids (it is below hydrogen in the electrochemical series). Concentrated sulfuric acid converts it into the sulfate, $Sb_2(SO_4)_3$, with liberation of sulfur dioxide, and nitric acid oxidizes it to the pentavalent condition, forming the solid H_3SbO_4.

When heated on charcoal with a blowpipe flame, the oxide Sb_2O_3 results, and forms a characteristic bluish-white film on the charcoal. Chlorine unites with it, forming the chloride $SbCl_3$.

Stibine ***(SbH_3)*** · The gas *stibine* (SbH_3) is formed under conditions which are very similar to those which produce arsine, and it resembles the latter compound, though it is less stable. It is very poisonous.

In Marsh's test for arsenic, any antimony that is present is converted into stibine, and this results in a black mirror deposit, as in the case of arsenic. The deposit is more sooty in appearance than is the arsenic deposit, and it is not dissolved by a solution of sodium hypochlorite, whereas the deposited arsenic is dissolved by this reagent.

Halogen Compounds of Antimony · Antimony forms an almost complete double series of halogen compounds, and the pentiodide alone is unknown. They can be prepared by direct union of the elements, and in some cases by the action of the halogen acid upon antimony or its oxides.

Oxides of Antimony · Antimony forms three oxides: Sb_2O_3, a white solid; Sb_2O_4, a white powder; Sb_2O_5, a yellow powder. The trioxide and pentoxide *are weak acid anhydrides and are capable of forming two series of acids, corresponding in formulas to the acids of phosphorus and arsenic.* They are much weaker, however, and are of little importance.

Sulfides of Antimony · Antimony resembles arsenic in that hydrogen sulfide precipitates it as a sulfide when conducted into an acid solution containing an antimony compound:

$$2\ SbCl_3 + 3\ H_2S \longrightarrow Sb_2S_3 \downarrow + 6\ HCl$$
$$2\ SbCl_5 + 5\ H_2S \longrightarrow Sb_2S_5 \downarrow + 10\ HCl$$

The two sulfides of antimony are called the trisulfide and the pentasulfide respectively. When prepared in this way they are orange-colored substances, though the mineral stibnite is black. The sulfides of antimony are used in the manufacture of matches and of red rubber.

Thio Salts of Antimony · Like the sulfides of arsenic, the sulfides of antimony dissolve in solutions of soluble sulfides and form the corresponding thio salts. Of these the best-known are *sodium thioantimonite* (Na_3SbS_3) and *sodium thioantimonate* (Na_3SbS_4).

Metallic Properties of Antimony · The fact that the sulfide of antimony is precipitated by hydrogen sulfide shows that the element can act as a metal in a chemical way. Its hydroxide, $Sb(OH)_3$, dissolves in acids, forming salts, and in such reactions acts as a base:

$$Sb(OH)_3 + 3\ HNO_3 \longrightarrow Sb(NO_3)_3 + 3\ H_2O$$

Many other reactions show that antimony has more of the chemical characteristics of a metal than of a nonmetal.

Amphoteric Hydroxides · While antimony hydroxide occasionally acts as a triacid base, as represented in the last paragraph, it usually loses water and forms the monohydroxide, or oxyhydroxide, SbO · OH:

$$Sb(OH)_3 \longrightarrow H_2O + SbO \cdot OH$$

This hydroxide differs from those we have considered in that it can act either as a weak acid or as a weak base, as indicated in the reactions

$$SbO \cdot OH + NaOH \longrightarrow SbO \cdot ONa + H_2O$$
$$SbO \cdot OH + HCl \longrightarrow SbO \cdot Cl + H_2O$$

The hydroxides of a number of the metals act in this same way and are called *amphoteric* hydroxides. *Amphoteric* comes from a Greek word meaning "both" and *an amphoteric hydroxide is one that can act either as a weak acid or as a weak base;* in other words, it can yield either hydrogen ions or hydroxyl ions.

The way in which an amphoteric hydroxide will act in a given case depends on the nature of the substance with which it is reacting. In the presence of *a base* (hydroxyl ions) its hydrogen ions are used up to form water, and its ionization is displaced toward the *acid* side, so that it be-

haves like a *weak acid.* Similarly, in the presence of *an acid* (hydrogen ions), it acts as a *weak base.*

Oxygen Acids Really Hydroxides · It may appear a little inconsistent to think of an acid as a *hydroxide,* but in reality nearly all oxygen acids, as well as all oxygen bases, are hydroxyl compounds. Thus, sulfuric acid is $SO_2(OH)_2$ (p. 385). The real distinction between an acid and a base is not a matter of the possession of hydroxyl groups, but of *the way the compound ionizes. If a hydroxyl compound gives hydrogen ions, it is an acid; if it gives hydroxyl ions, it is a base.* As a rule, metallic hydroxides are bases, whereas the hydroxides of nonmetals are acids.

Hydrolysis of Antimony Salts · Since antimony hydroxide ($Sb(OH)_3$) acts as a very *weak* base, we should expect its salts to be hydrolyzed by water (p. 457). If antimony chloride were to be *completely* hydrolyzed, like phosphorus trichloride, the equation might be written as follows:

$$SbCl_3 + 3\ H_2O \longrightarrow Sb(OH)_3 + 3\ HCl$$

But the reaction as written is not correct, as only two of the three chlorine ions are replaced:

$$SbCl_3 + H_2O \longrightarrow SbOCl\downarrow + 2\ HCl$$

The oxychloride (SbOCl), which precipitates as a white voluminous solid, may be regarded formally as arising by the loss of water from an intermediate $Sb(OH)_2Cl$. The oxychloride in turn may be still further hydrolyzed by the action of a large excess of water. If we wish to prevent this hydrolysis, we must add hydrochloric acid in sufficient quantity to reverse the reaction of hydrolysis.

The Antimonyl Radical (SbO) · The oxychloride SbOCl may be regarded as a salt of hydrochloric acid, the hydrogen atom of the acid having been replaced by the univalent *radical* SbO. This same radical is present in other salts and termed *antimonyl.* Thus, the common *tartar emetic,* used so largely in medicine, is a salt of tartaric acid ($H_2C_4H_4O_6$) and has the formula $K(SbO)C_4H_4O_6$. Its chemical name is, therefore, *potassium antimonyl tartrate.*

Bismuth

Occurrence · Bismuth is sometimes found in the uncombined form in nature. It also occurs as oxide and sulfide and as a constituent of many rare minerals. Most of the bismuth of commerce comes from Peru, Mexico, and Canada, the production in the United States being largely restricted to the metal recovered as a by-product in refining lead. It is not an abundant element.

Preparation · Bismuth is prepared by merely heating the ore containing the native bismuth and allowing the metal to run out into suitable vessels. Other ores are converted into oxides and reduced by heating with carbon. It is difficult to prepare the metal in a high state of purity.

Physical and Chemical Properties · Bismuth is a silvery metal with a decidedly ruddy tint. It is very crystalline and brittle, and has a high luster. Its density is 9.80, its melting point is 271°, and its boiling point is approximately 1450°.

Bismuth dissolves in hot, concentrated sulfuric and nitric acids to form bismuth salts, and it is very slowly attacked by hydrochloric acid in the presence of air. The halogen elements combine directly with it, but not with great energy.

At ordinary temperatures bismuth is not affected by air, but when heated it burns to form the yellow trioxide Bi_2O_3, which is also obtained by heating the hydroxide or carbonate. The chief sulfide of bismuth has the formula Bi_2S_3. It can be prepared by direct union of the elements or by conducting hydrogen sulfide into a solution of a bismuth salt:

$$2\ BiCl_3 + 3\ H_2S \longrightarrow Bi_2S_3\downarrow + 6\ HCl$$

Prepared in this latter way it is a black, amorphous precipitate.

Uses · Bismuth is used chiefly in the making of alloys and pharmaceutical preparations. The element, as well as its alloys, expands on cooling, and the alloys have low melting points. They will be referred to in connection with the metals.

Hydrolysis of Bismuth Salts · While the normal salts are stable in solutions containing an excess of acid, they are hydrolyzed in water or even in dilute acids. In this hydrolysis a basic salt is formed and not the hydroxide. With the chloride the reaction is expressed in the following equation:

$$BiCl_3 + H_2O \longrightarrow BiOCl\downarrow + 2\ HCl$$

This insoluble oxychloride may be regarded as the chloride of the base $BiO \cdot OH$, in which the group BiO plays the part of a univalent radical. This radical is called *bismuthyl*, just as the corresponding antimony radical is called *antimonyl*. There are, therefore, two series of salts: the normal salts, corresponding to the formulas $BiCl_3$ and $Bi(NO_3)_3$, and the bismuthyl salts (really basic salts), such as the chloride, BiOCl, the nitrate, $BiONO_3$, and the carbonate, $(BiO)_2CO_3$. A number of these bismuthyl salts, particularly the nitrate and the carbonate, are used in medicine. They are usually called *bismuth subnitrate* and *bismuth subcarbonate.*

QUESTIONS

1. The elements of the nitrogen family have similar electron configurations. (*a*) Should you expect them to form similar compounds? to have similar properties? (*b*) Why, then, is nitrogen a nonmetal and bismuth a metal? (*c*) Why is the hydroxide of nitrogen acidic, but the hydroxide of bismuth basic?

2. Why should the arsenic acids be weaker than the phosphoric acids? Relate your answer to the relative electron affinity of the atoms.

3. (*a*) In the table below are given the formulas for a hydride, oxide, chloride, and hydroxide of nitrogen. In the blank spaces write the formulas of the compounds that you would expect the other elements to form. (*b*) Explain the reason for any discrepancies between your predicted formulas and the known formulas.

	NITROGEN	PHOSPHORUS	ARSENIC	ANTIMONY	BISMUTH
Hydride	NH_3				
Oxide	N_2O_5				
Chloride	NCl_3				
Hydroxide	NO_2OH				

4. (*a*) What properties of ammonia make it useful as a refrigerant? (*b*) How do you explain the fact that an aqueous solution of ammonia reacts as a base?

5. Explain, with the use of Le Châtelier's principle, the fact that optimum yields of ammonia are obtained in the Haber process when the mixture of nitrogen and hydrogen is subjected to *high* pressures (pp. 181, 397).

6. Zinc is above hydrogen in the electrochemical series. Why, then, is hydrogen not evolved when zinc is dissolved in dilute nitric acid?

7. What explanation can you offer for the great difference between white phosphorus and violet (or red) phosphorus?

8. What economic advantages can you suggest for preparing pure (100 per cent) phosphoric acid by burning phosphorus vapor, as compared with oxidizing solid phosphorus with nitric acid?

9. What are the meanings of the prefixes *ortho-*, *meta-*, and *pyro-*, as applied to the acids of phosphorus?

10. (*a*) H_2S and H_2Se are decomposed by heat, just as AsH_3 is. What should you expect to find if these gases were to be treated like AsH_3 in a Marsh test? (*b*) Would the presence of sulfides in the zinc used in the Marsh apparatus interfere with a test for arsenic?

11. Why should you expect NCl_3 to hydrolyze completely but $BiCl_3$ only partially?

12. (*a*) What is an acid anhydride? (*b*) Write the equations for the reactions, with water, of the acid anhydrides found in this chapter.

13. Balance the following equations, using the method of electronic partial equations and the oxidation-state method:

a. $Cu + HNO_3 \longrightarrow$
b. $CuS + HNO_3 \longrightarrow$
c. $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NH_4NO_3 + H_2O$
d. $Sn + HNO_3 + H_2O \longrightarrow H_2SnO_3 + NO$
e. $Bi + HNO_3 \longrightarrow Bi(NO_3)_3 + NO + H_2O$
f. $As_2S_3 + H_2O + HNO_3 \longrightarrow H_3AsO_4 + NO + S$
g. $Ag + HNO_3 \longrightarrow AgNO_3 + NO + H_2O$

14. Show, by equations, how you can prepare (*a*) ammonium chloride from ammonia; (*b*) nitric acid from ammonia; (*c*) nitrous oxide from sodium nitrate; (*d*) ferric nitrate from iron; (*e*) sodium nitrate from sodium chloride.

15. Give the meaning of the following terms: (*a*) *nitrogen fixation;* (*b*) *ammonia liquor;* (*c*) *Haber process;* (*d*) *Birkeland-Eyde process;* (*e*) *condensed acid;* (*f*) *complex ion;* (*g*) *thioacid;* (*h*) *superphosphate;* (*i*) *Marsh test.*

16. Given the following substances and no others air, bismuth, calcium phosphate, hydrochloric acid, sodium hydroxide, sulfuric acid, water show, by writing equations for the reactions which take place, how you could prepare (*a*) $(NH_4)_2SO_4$; (*b*) NH_4NO_3; (*c*) NO; (*d*) NaH_2PO_4; (*e*) BiOCl. (Write a separate equation for each step.)

17. What should you expect to obtain by crystallizing a mixture of trisodium phosphate and monosodium phosphate from a water solution?

18. What should you expect to get by heating arsenic pentoxide with hydrochloric acid?

19. How can you produce the following changes: (*a*) $P \longrightarrow P_4O_{10} \longrightarrow H_3PO_4 \longrightarrow Na_2HPO_4 \longrightarrow Na_4P_2O_7$; (*b*) $As \longrightarrow As_2O_3 \longrightarrow As_2S_3 \longrightarrow Na_3AsS_3 \longrightarrow As_2S_3$; (*c*) $Bi \longrightarrow Bi_2O_3 \longrightarrow BiCl_3 \longrightarrow BiOCl \longrightarrow Bi_2S_3$? (Write equations for all the reactions which take place.)

PROBLEMS

1. A certain phosphate rock was found to contain 80 per cent calcium phosphate. (*a*) What weight of phosphorus can be prepared from 1000 kg of this rock? (*b*) What weight of phosphoric acid?

2. Suppose you were to prepare 100 g of metaphosphoric acid, starting with phosphorus. (*a*) Write equations for the reactions involved. (*b*) What weight of phosphorus would be required?

3. Suppose the poisonous qualities of Paris green and Scheele's green are proportional to the combined percentages of arsenic and copper in these compounds. Which one should be the more poisonous?

4. If the formula of bismuthyl carbonate is assumed to be $(BiO)_2CO_3$, what weight of bismuth will be required to make 100 g of the compound?

5. If the black mirror deposit in the tube of a Marsh-test apparatus should be found to weigh 30 mg, what weight of "white arsenic" would be in the sample analyzed?

6. If a superphosphate fertilizer consists of a mixture of $Ca(H_2PO_4)_2$ and 2 $CaSO_4$, as shown by the equation on page 418, to what per cent of P_4O_{10} would it be equivalent?

7. What weight of P_4O_{10} must be used in order to prepare 400 ml of 0.2 *N* H_3PO_4?

8. What volume of ammonia gas, measured under standard conditions, will be required to form $(NH_4)_3PO_4$ with 500 ml of 1.5 *N* H_3PO_4?

9. What volume of 0.4 *N* NaOH will be required to neutralize 40 ml of 0.3 *N* HNO_3?

10. Forty grams of phosphorus reacts completely with 51.6 g of oxygen to form an oxide. What is the ratio of atoms in the oxide?

CHAPTER 24

RATE OF REACTION; EQUILIBRIUM

Introduction · The main factors that influence the rate (or velocity, or speed) of a chemical reaction have already been briefly outlined in Chapter 5; and the general idea of equilibrium as a balance between two changes opposing each other has been suggested in a number of instances in the foregoing pages. It is now desirable to consider these important subjects somewhat more in detail.

Rate of a Reaction · By the *rate* of a reaction is meant the mass of material undergoing transformation in a unit of time, such as a second, a minute, or an hour. In an entirely similar way we should say that the rate of mining coal is measured by tons mined per day. The mass transformed in a chemical reaction, in a definite time interval, can usually be measured. The rate of gas evolution, for example, may be measured (Fig. 24-1), or the amount of acid formed can be determined by titration with a base, or the change in pressure resulting from the chemical transformation of gases may be observed.

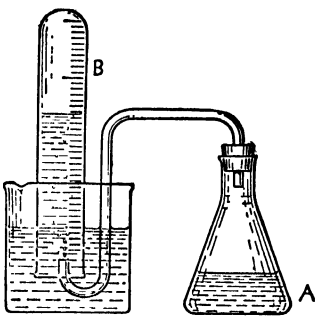


Fig. 24-1. Measuring the Rate of a Reaction in Which an Insoluble Gas Is Generated The reaction is carried out in the flask, *A*, and the rate of reaction is noted by the volume of gas collected in *B* in unit time

It will help us in our understanding of the various factors controlling the rate of a reaction if we realize, in the beginning, that atoms, ions, and molecules do not react chemically with one another at a distance, but must come quite close together in collisions. It is generally only in this way that atoms can be gained or lost and that the switching of partners (an act common to many reactions) can occur.

Factors Which Influence the Rate of a Reaction · The important general factors which determine whether a reaction is to be fast or slow are (1) the nature of the reacting substances, (2) temperature, (3) catalysis, and (4) concentration. Let us now consider these separately.

1. **Nature of reacting substances.** As would be expected, different substances react with each other at different rates. An extreme example of this is given by the difference between the rates of reaction of electrovalent and covalent substances, as discussed in Chapter 13. As fast as

the ions of the former are mixed together—in solution, for instance—so that they can collide, they tend to attract one another and combine. On the other hand, reactions involving *covalent molecules* generally proceed much more slowly, and often at a conveniently measurable rate. It is only this latter type of reaction which will be discussed in what immediately follows.

2. **Temperature.** A rise in temperature greatly increases the rate of a reaction. As a rough approximation, it may be stated that a rise of 10° about doubles the rate. If, therefore, a reaction is proceeding at a certain rate at 0°, it will go twice as fast at 10° and four times as fast at 20°. At 50° its speed will be 32 times as great as at 0°. Reactions whose speed is imperceptible at any ordinary temperature (for example, the oxidation of coal) may therefore become very rapid at a temperature within the reach of a Bunsen burner. On the other hand, we can greatly retard a reaction by keeping the material cold, as when we put food in cold storage in order to slow down the putrefying reactions which result in spoilage.

Why does the reaction rate increase 100 per cent when the temperature is raised 10°? The number of collisions between reactant molecules increases as the temperature rises, because of the greater velocity with which the molecules move (p. 76); but for a rise of 10° the increase in number of collisions is only a few per cent. The real explanation involves the fact that molecules must not only collide, but collide with a characteristic *minimum violence* if their covalent bonds are to be broken and reaction is to take place. While the average energy of the molecules is not increased greatly by a given rise in temperature, the number of molecules with exceptionally high energies increases very markedly, as indicated in the discussion of vapor pressure in Chapter 11. A rise of 10° just about doubles the fraction of the molecules which possess enough energy to be *activated*, or "ripe," for reaction as collisions occur, and so the reaction rate is approximately doubled.

3. **Catalysis.** The increase of reaction rate in the presence of a suitable catalyst has already been mentioned in several instances (pp. 48, 97). A catalyst is generally supposed merely to modify the rate of a reaction which is already capable of taking place spontaneously without the catalyst. No energy is contributed by the catalyst to the reaction. In increasing the rate the catalyst may be said to function somewhat as a lubricant; but just how a catalyst performs its function is not very well understood.

Without doubt catalysts exert their influence in a variety of ways. Some appear to form, with one or more of the reacting substances, a definite but unstable compound, which later undergoes decomposition or

reaction of some sort and yields the product and at the same time restores the catalyst, which may then act over again.

Other catalysts seem to owe their efficiency to their very large surface, on which molecules of the reacting substances may become attached, or *adsorbed*, and thus be brought very intimately into contact. An excellent illustration of this effect is to be found in the manufacture of sulfuric acid by the *contact process*. Sulfuric dioxide and oxygen react very slowly to form sulfur trioxide:

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$

But in the presence of *metallic platinum*, upon the surface of which the molecules of both SO_2 and O_2 are adsorbed, the reaction proceeds with great rapidity.

Catalyst poisons. In the reaction that we have just been considering, it is important that the sulfur dioxide gas and oxygen which are brought into contact on the platinum be very pure. Certain impurities, especially arsenic, even in extremely small traces, will cover up, or "poison," the platinum surface in such a way that there is no longer any available space upon which the molecules SO_2 and O_2 can "sit down."

4. **Concentration.** Since a reaction takes place between individual molecules, and since these cannot act upon one another at a distance, it will be seen that any condition which increases the number of collisions in unit time will increase the speed of the reaction. The more reactant molecules there are crowded into a given volume,—that is, the greater the concentration,—the better is the chance that molecules of one kind will find molecules of another kind with which they may react. It is a question of probability. It is probable that a hundred boys, all blindfolded and wandering about on a small dance floor in a perfectly random fashion, would collide with one another far more frequently than if they were moving about in the same way in the much larger space of a football field.

The Law of Mass Action · As early as the beginning of the nineteenth century, Berthollet made important measurements on the effect of concentration, but it was not until 1867 that the dependence of the rate of reaction on concentration was definitely understood. In this year the Norwegian scientists Guldberg and Waage formulated and published the results of their investigations in the form of the *law of mass action*, which states that *the rate of a reaction is proportional to the active mass of each of the reacting substances*. By "active mass" Guldberg and Waage meant what we define as *concentration*, the quantity present in a given volume, which determines the "crowdedness" of the molecules. Any units may

be used to express concentration, as grams per liter or gram-molecular weights per liter or pounds per cubic foot.

Concentration Expressed as Gram-Molecular Weights per Liter · For the sake of convenience and especially for the sake of being able to keep track of the actual numbers of reactant molecules taking part in a reaction, we nearly always express concentration in terms of gram-molecular weights per liter (and measure the rate as the number of gram-molecular weights transformed per liter per minute or per second). We know, of course, that a gram-molecular weight of any substance contains the Avogadro number ($N = 6.02 \times 10^{23}$) of molecules. Usually the chemical reactions in which we are most interested take place in solution, although many common reactions occur between gas molecules. In both cases the concentration is expressed, as just indicated, as *molar* concentration (p. 198).

Illustration · Let us consider the reaction between gaseous hydrogen and gaseous iodine to form hydrogen iodide:

$$H_2 + I_2 \longrightarrow 2\ HI$$

The rate of this reaction, according to the law of mass action, is proportional to the concentrations of both hydrogen and iodine. Introducing a proportionality constant, we may write

$$\text{Rate} = k \times [H_2] \times [I_2],$$

where [ ] is a symbol meaning "the molar concentration of."

In *actual magnitude* the rate will also depend upon the temperature, the presence of catalysts, and the properties of the reacting substances. At a given temperature and with a given chemical reaction, all these influences are constant in value; and we may designate their combined effect by the constant k, which is called the *rate constant* or *velocity constant* at that temperature.

Evaluation of k · The numerical value of k is determined by measuring the rate of reaction when the concentrations are known. If, for example, we put a 1-liter vessel into a furnace maintained at 410°, evacuate it, introduce $0.01 \times 6.02 \times 10^{23}$ molecules of both hydrogen and iodine (making the concentration of each 0.01 molar), and measure the amount of hydrogen iodide formed in the initial stages of the reaction, we find that 0.00015 g-mol. wt of hydrogen iodide is formed per minute. Since the volume of the vessel is 1 liter and the concentrations are 0.01 molar, the value of k is obtained by solving the expression

$$0.00015 = k \times 0.01 \times 0.01,$$

whence $k = 1.5$.

Calculation of Rate from k · Once k has been determined by measuring the rate at a known concentration, the rate at the same temperature for any other concentration may be predicted and verified. For example, if in a new experiment the concentration of hydrogen is made 0.02 molar, that of iodine being left at 0.01 molar, and the initial rate is measured, it is found to be 0.00030 g-mol. wt/liter/minute, corresponding to the value predicted from the product $1.5 \times 0.02 \times 0.01$. Similarly, if the concentrations of both hydrogen and iodine are made equal to 0.02 molar, the initial rate is found to be 0.00060 g-mol. wt/liter/minute, which is four times that of the original experiment, corresponding to the product $1.5 \times 0.02 \times 0.02$.

Effect of Temperature Changes on k · All these experiments are carried out at the same temperature. At a higher temperature, 427°, the value of k is found to be 3.8. At the concentrations considered above, therefore, the rates would be 0.00038, 0.00076, and 0.00152 g-mol. wt of hydrogen iodide formed per liter per minute.

Other factors affecting reaction rate. In addition to the four generally important factors which we have just been discussing, there are others which occasionally, in particular cases, exert a profound influence on the rate of a reaction. For instance, *radiant energy* will cause certain chemical changes to occur. In visible light photosynthesis (p. 108) takes place, and a photographic film is affected; ultraviolet light burns our skin; X rays and gamma rays decompose cancer cells. In all such photochemical reactions the rate depends on the intensity of the light. Then, too, certain inactive molecules may be *activated* by *bombardment* with alpha particles, electrons, or other fast-moving particles, or by the effects of a *silent electric discharge*, as in the formation of ozone. The rate of a reaction may be greatly affected by the nature of the *solvent* in which the reaction is taking place. Also, the rate of reactions involving solids may depend on the *degree of subdivision* of the solids.

Reversible Reactions · Many chemical reactions are reversible to a measurable extent; the products of a reaction react with one another to form the original substances. This is true of the hydrogen iodide reaction; molecules of hydrogen iodide, as they are formed, react again to form hydrogen and iodine. Reversibility is commonly indicated in equations by writing two arrows, one pointing to the right and the other to the left:

$$H_2 + I_2 \rightleftarrows 2\ HI$$

The rate of the reverse reaction is governed by the law of mass action also; it is proportional to the concentrations of the reacting substances, which are now 2 hydrogen iodide molecules:

$$\text{Rate of reverse reaction} = k' \times [HI] \times [HI] = k' \times [HI]^2,$$

where k' is, of course, a proportionality constant different from that for the forward reaction. Its numerical value at 410° is found by experiment to be 0.031 when concentrations are measured in gram-molecular weights per liter and time is measured in minutes.

Note that the concentration of hydrogen iodide appears as the square, since two molecules enter into the reaction; the coefficients which show the number of the reactant molecules in the chemical equation are usually to be used as exponents for the concentrations in the mass-action equation.

Complex Reactions · The rate of a reaction is not necessarily dependent upon the concentrations of all the substances whose formulas appear in the equation for the reaction. The reason for this is that the final products are sometimes formed by a series of reactions in which intermediate substances are first formed, which then react further to form the final products. The law of mass action must then be applied separately to each of the reactions in the series, giving as many rate equations as there are reactions. If one of the reactions in the series is slower than the rest, then the rate of product formation is determined by the rate of this slowest, *rate-determining step*, and the concentrations of only those substances which appear in the equation for this step determine the rate of formation of the final products.

In cases of catalysis in solution, the rate depends upon the concentration of the catalyst, even though the formula of the catalyst does not appear in the equation for the reaction. For example, the decomposition of hydrogen peroxide is expressed by the equation

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

In the presence of bromide ion, which acts as a catalyst, the rate does not depend upon the square of the concentration of hydrogen peroxide, as might be expected, but is found experimentally to depend upon the product of the concentrations of hydrogen peroxide and bromide ion:

$$\text{Rate} = k \times [H_2O_2] \times [Br^-]$$

The explanation of this experimental finding is that the reaction proceeds in steps, of which the slowest and rate-determining step is the reaction between hydrogen peroxide and bromide ion. Following rapidly upon this reaction must be other rapid steps in which bromide ion is regenerated (bromide ion is a catalyst and does not suffer any permanent change) and in which a second molecule of hydrogen peroxide is used. Information other than that obtained from measurements of the rate of the reaction is necessary in order to decide exactly what these additional steps are.

Equilibrium · It is evident that the rate of a reaction must be expected to decrease as the reaction proceeds. For, as a result of the reaction, the concentration of the reactants steadily decreases, since they react to form products; by the law of mass action the decrease in concentration results in a decrease in the reaction rate, which approaches zero as the original material is used up. In a reversible reaction, however, the concentration of the original reactants does not drop to zero, since they are continuously being formed by the reverse reaction. The starting substances react with one another to form the products; and then the products, if they are not allowed to escape from the scene of action, react to give back the starting substances, at least to a certain extent. In the early stages the forward reaction has its greatest rate, and then gradually becomes slower as the reactants are used up. On the other hand, the reverse reaction is relatively extremely slow in the beginning; but as the concentration of the products builds up, it becomes faster and faster. Eventually the forward reaction (as it is written in a chemical equation) and the reverse reaction come to the same rate. This state of affairs, when the rates of the two opposing reactions have become equal, is called an equilibrium. No further net transformation takes place, since the molecules of the reactants are formed by the reverse reaction as fast as they are used up by the forward reaction. Although no reaction seems to be taking place, actually both reactions continue, but at equal rates.

Evidence for Continuance of Reactions at Equilibrium · While we have been quite sure that at equilibrium the two opposing reactions continue steadily at equal rates, until recently we have had no definite experimental method for proving that this is true. Neither the composition nor the concentration of anything taking part in the opposing reactions undergoes change when equilibrium has been established; so what can be measured to prove that the reactions are still going on? We shall have to tag the atoms themselves in a compound on one side of the equation and see whether any of them presently turn up in compounds on the other side. Now this is just what has been done, in the following way:

1. In solution arsenious acid is known to be slowly oxidized to arsenic acid by iodine, and an equilibrium is presently reached, as expressed in the equation

$$\underset{\text{arsenious acid}}{H_3AsO_3} + \underset{\text{iodine}}{I_2} + H_2O \rightleftarrows \underset{\text{arsenic acid}}{H_3AsO_4} + \underset{\text{hydriodic acid}}{2\,HI}$$

2. When equilibrium has been reached, the concentration of each of the participants in the reaction is carefully measured.

3. Arsenious acid is then prepared *that is radioactive*. This is done by bombarding arsenious acid (or the arsenic from which it is made) with neutrons (see page 356). This radioactive arsenious acid behaves exactly like ordinary arsenious acid in its chemical action.

4. A solution is now prepared in such a way that the concentrations of iodine, water, hydriodic acid, arsenic acid, and arsenious acid are exactly those found to be present at equilibrium in No. 2. However, *radioactive arsenious acid* is used instead of the ordinary acid.

5. If opposing reactions *stop* when equilibrium has been reached, the radioactive arsenious acid will be unchanged, and none of the *arsenic* acid will become radioactive.

6. After a time the arsenic acid is removed from the solution (by precipitation), tested with an electroscope (p. 321), *and found to be radioactive,* and to just the extent required by the calculated speed of the direct reaction.

This shows that *at equilibrium* the radioactive arsenious acid is being oxidized to give radioactive arsenic acid, and, since none of the concentrations change, the reverse reaction is also going on. In other words, an equilibrium is dynamic, not static.

Example of the Approach to Equilibrium · The table below shows the changes in rate and concentration for the reversible formation and decomposition of hydrogen iodide at 410°. The experiment

$$H_2 + I_2 \rightleftarrows 2\,HI$$

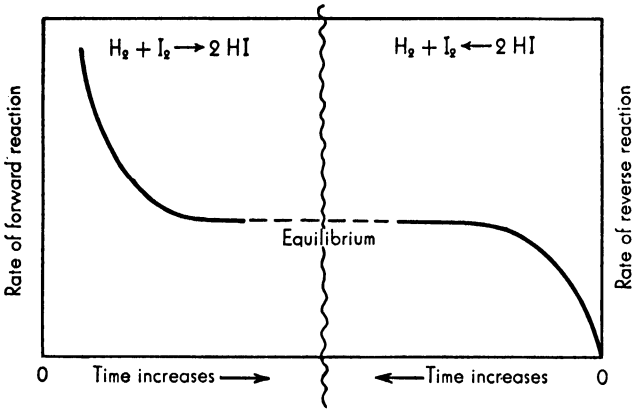
started with 0.01 molar hydrogen and iodine; the various columns show how the rate of the forward reaction decreases and that of the reverse

RATES OF THE REACTIONS INDICATED BY $H_2 + I_2 \rightleftarrows 2\,HI$

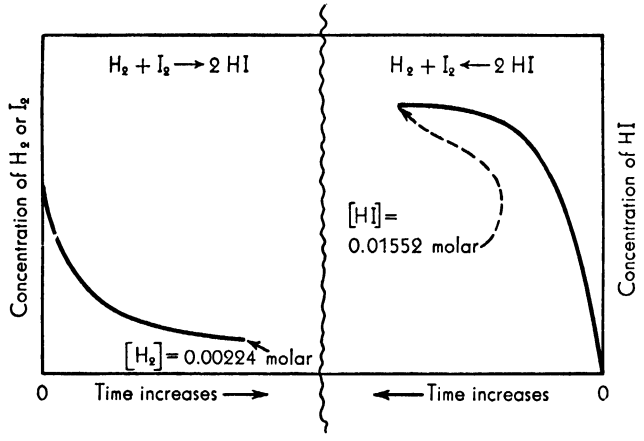
TIME (MINUTES)	CONCENTRATION OF HYDROGEN (AND OF IODINE) (MOLAR)	RATE OF FORWARD REACTION (G-MOL. WT/LITER/MIN)	RATE OF REVERSE REACTION (G-MOL. WT/LITER/MIN)	CONCENTRATION OF HYDROGEN IODIDE (MOLAR)
0	0.0100	0.000150	0	0
34	0.0080	0.000096	0.0000005	0.0040
90	0.0060	0.000054	0.0000020	0.0080
220	0.0040	0.000024	0.0000045	0.0120
470	0.0030	0.0000135	0.0000061	0.0140
960	0.0023	0.0000079	0.0000073	0.0154
1400	0.00225	0.0000076	0.0000074	0.0155
Very long	0.00224	0.0000075	0.0000075	0.01552

reaction increases as the reaction proceeds, together with the changes in concentration of hydrogen and hydrogen iodide which cause these changes in rate. These data are plotted in Fig. 24-2 (p. 440).

It is seen (in the table above and in Fig. 24-2) that the rates of the two opposing reactions gradually approach each other and become equal at equilibrium. When equilibrium has been reached, the concentrations of hydrogen and iodine have been reduced to 0.00224 molar, and the concentration of hydrogen iodide is 0.01552 molar. It is sometimes convenient to indicate the *position of equilibrium* in terms of the relative amounts of reactants and products. Thus, for the hydrogen iodide reac-



Graph of changes in the rates of the reactions



Graph of changes in concentrations

Fig. 24-2. Approach to Equilibrium in the Formation and Decomposition of Hydrogen Iodide: $H_2 + I_2 \rightleftarrows 2\,HI$

tion at 410°, the position of equilibrium is on the side of the hydrogen iodide; that is, the concentration of hydrogen iodide at equilibrium is greater than the concentration of the reactants.

Effect of Changes in Concentration on Equilibrium · If more of one of the reacting substances is added to a system in equilibrium, the rate of the reaction involving that substance is increased. Equilibrium is re-established when the concentration of reactants has been reduced (by reaction to form products), and thereby the rate of the forward reaction reduced, and when the rate of the reverse reaction has increased (as a result of the increase in the concentration of products) to such a point that the two rates are again equal. At equilibrium, however, the rates of

both reactions are greater than they were in the original equilibrium, before the addition of more reagent; correspondingly, the concentration of reaction products is greater than before. The result of the addition of more reactant has been to increase the concentration of reaction products, and we say that the position of equilibrium has been shifted toward the products.

Illustration · If to the equilibrium mixture of hydrogen, iodine, and hydrogen iodide reached in the table on page 439,

$$[H_2] = [I_2] = 0.00224 \text{ molar}, \quad [HI] = 0.01552 \text{ molar},$$

is added additional iodine to increase the iodine concentration to 0.01225 molar, the rates and concentrations will change as indicated in the following table:

EFFECT OF INCREASED IODINE CONCENTRATION ON THE EQUILIBRIUM $H_2 + I_2 \rightleftarrows 2\,HI$

TIME AFTER ADDITION OF IODINE (MINUTES)	CONCENTRATION OF IODINE (MOLAR)	CONCENTRATION OF HYDROGEN (MOLAR)	RATE OF FORWARD REACTION (G-MOL. WT/LITER/MIN)	RATE OF REVERSE REACTION (G-MOL. WT/LITER/MIN)	CONCENTRATION OF HYDROGEN IODIDE (MOLAR)
0	0.01225	0.00224	0.000041	0.0000075	0.01552
62	0.0115	0.00149	0.000026	0.0000090	0.01702
140	0.0110	0.00099	0.000016	0.0000101	0.01802
260	0.0108	0.00079	0.000012	0.0000105	0.01842
440	0.0107	0.00069	0.000011	0.0000107	0.01862
Very long	0.010685	0.000675	0.0000108	0.0000108	0.01865

Note that the rates at equilibrium, while again equal, are greater than previously (table on page 439), and that the concentration of hydrogen iodide at equilibrium is greater, and the concentration of hydrogen less, than before, which confirms the predicted shift in the position of equilibrium toward hydrogen iodide. These changes are shown graphically in Fig. 24-3 (p. 442).

Le Châtelier's Principle · The effect on the position of equilibrium resulting from changing the concentration of one of the substances present in an equilibrium reaction is a special case of one of the most far-reaching generalizations of chemistry and physics, first stated by Le Châtelier in 1887 (Chap. 11). Le Châtelier's principle may be stated as follows: *If a stress is applied to a system in equilibrium, the position of equilibrium will shift in such a direction as to diminish the applied stress.* In the case discussed above, the stress applied is the addition of more reactant; in order to diminish the stress the system tends to reduce the concentration of the added substance. It can do this only by allowing that substance to react; as a result of this reaction, more of the product

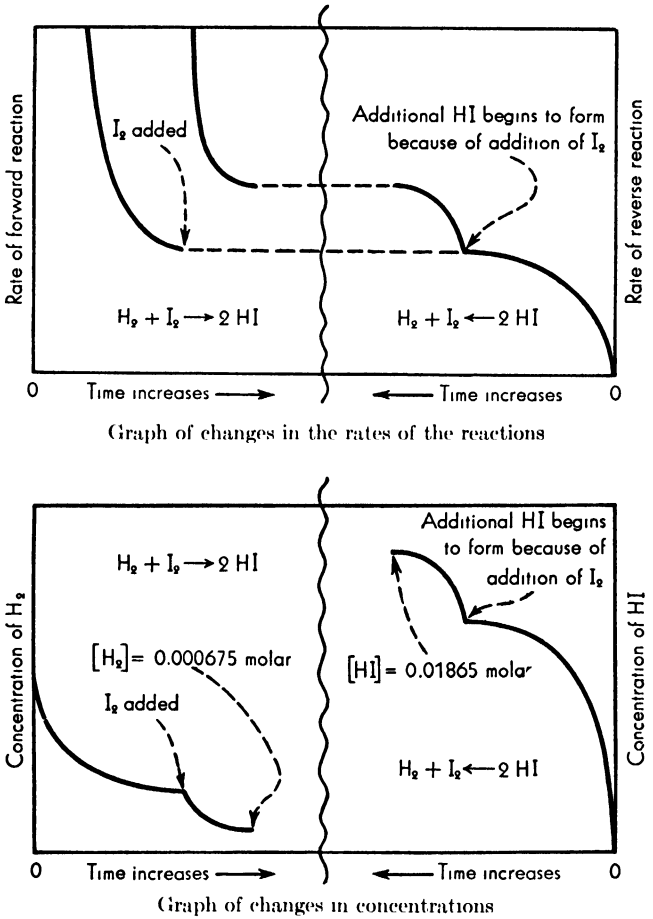


Fig. 24-3. The Change in the Position of the Equilibrium $H_2 + I_2 \rightleftarrows 2\ HI$, Resulting from the Addition of Iodine to the Equilibrium Mixture Shown in Fig. 24-2

is formed, and when the new equilibrium is established, the position of equilibrium has shifted toward the products.

Predictions from Le Châtelier's Principle · The effect of concentration changes discussed above is one example of the applicability of Le Châtelier's principle. Many other changes in environment can also affect the position of equilibria, both physical and chemical. Some illustrations of these have been mentioned in Chapter 11; others are given below.

1. Just as the addition of excess reactant will cause the position of equilibrium to shift toward the products, so the addition of product will drive the equilibrium the other way.

2. If ice, in equilibrium with water, is subjected to a definite pressure, it will melt because a given weight of water occupies less volume as a liquid than as a solid. As the ice melts, the pressure is relieved.

3. Similarly the application of pressure to a mixture of hydrogen, nitrogen, and ammonia gases in equilibrium,

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

will shift the position of equilibrium to the right. The volume occupied by the $2 \times 6.02 \times 10^{23}$ molecules of ammonia ($2\ NH_3$) will be only one half that required by the $4 \times 6.02 \times 10^{23}$ molecules ($N_2 + 3\ H_2$) on the left (Avogadro's law); in order to relieve the pressure increase, the system shrinks to a smaller volume by forming more ammonia.

4. Substances which dissolve with the absorption of heat (as most substances do) will become more soluble as the temperature is raised. More of the substance will dissolve to absorb the applied heat. This has been observed in Chapter 12.

5. All chemical reactions involve changes in energy, and in a chemical equilibrium one reaction evolves energy while the reverse reaction absorbs energy. To increase the temperature favors the heat-absorbing reaction. For example, the equilibrium

$$2\ H_2 + O_2 \rightleftarrows 2\ H_2O + \text{heat}$$

shifts toward the left if the temperature is increased.

Importance of Equilibria and Reaction Rates in Industrial Processes · One of the tasks of the chemical engineer is to take a reaction which can be made to occur in the laboratory and carry it out on a large scale under such conditions that the products of the reaction can be marketed at a profit. This usually involves a careful study of the position of equilibrium under different conditions and of rates of reaction. Given certain starting materials, profitable operation may require a nice balance between rate of reaction, position of equilibrium, cost of equipment, etc.

The operation of these features may be illustrated by considering the preparation of ammonia by the Haber process (page 397). The reaction is

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3 + 22{,}000\ \text{cal}$$

It is evident from Le Châtelier's principle that the position of equilibrium will be most favorable at low temperatures and high pressures, and this is borne out by the first figure in the upper right-hand corner of the table on page 444, which shows that at 200° and 1000 atm there is 98 per cent of ammonia present in the equilibrium mixture formed when 1 g-mol. wt of nitrogen and 3 g-mol. wt of hydrogen react. As the pressure decreases

from 1000 atm, the position of equilibrium shifts toward the left, the change taking place in the direction opposite to that for the increase in pressure discussed in No. 3 above. As the temperature increases, the position of equilibrium also shifts toward the left, according to the principle discussed in No. 5 above. In spite of these facts, the Haber process does not operate at 200° and 1000 atm, but at 500° and 200 atm, where the percentage of ammonia at equilibrium is only 17 per cent.

The reason for this is that the chemical engineer must consider reaction rates and equipment costs, as well as the position of equilibrium. At 200° the rate of formation of ammonia is so slow that it would not be worth while to build a plant to make it. The rate can be increased by adding a catalyst and by increasing the temperature. The addition of a catalyst alone is not sufficient; so the engineer is forced to raise the temperature, even though this makes the position of equilibrium unfavorable, and chooses then the lowest temperature at which, with a catalyst, the reaction takes place at a reasonable rate. Although, even at 500°, the yield is considerably better the higher the pressure, the capital investment and operating costs also increase with the pressure, since the equipment must be sturdier to withstand the pressures, more power is needed for the compressors, etc. When the increased yield is balanced against these factors, it is found that a lower yield at a lower pressure is more economical, and the plant is operated at 200 atm. The waste of unreacted nitrogen and hydrogen is avoided by removing the ammonia from the gases after passage through the catalyst bed, and recycling the unreacted components.

PERCENTAGE OF AMMONIA PRESENT AT EQUILIBRIUM IN AN ORIGINAL MIXTURE OF 1 G-MOL. WT OF NITROGEN AND 3 G-MOL. WT OF HYDROGEN AT VARIOUS PRESSURES AND TEMPERATURES

TEMPERATURE	1 ATM	50 ATM	100 ATM	200 ATM	600 ATM	1000 ATM
200°	15.3%	74.4%	81.5%	85.8%	95.4%	98.3%
400°	.48%	15.3%	25.1%	36.3%	65.2%	79.8%
500°	.13%	5.6%	10.6%	17.6%	42.2%	57.5%
600°	.05%	2.25%	4.5%	8.2%	23.1%	31.4%
800°	.022%	.57%	1.19%	2.2%	—	—
1000°	.004%	.21%	.45%	.9%	—	—

Equilibrium Constant · The position of equilibrium in a reversible reaction may be calculated from a knowledge of the equilibrium constant for the reaction. This may be derived as follows: Let us set up a very general equation for a chemical reaction, in which the substances A and B react to form the products C and D:

$$A + B \rightleftarrows C + D$$

At equilibrium the forward rate = the backward rate. But the forward rate = $k \times [A] \times [B]$, and the backward rate = $k' \times [C] \times [D]$. Therefore, since things equal to the same thing are equal to each other, it follows that

$$k \times [A] \times [B] = k' \times [C] \times [D].$$

This equation may be rearranged to the form

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{k}{k'} = K,$$

where the ratio of the two velocity constants, k and k', is equal to another constant, K, called the *equilibrium* constant.

The equilibrium constant may be defined as the product of the molar concentrations of the reaction products at equilibrium divided by the product of the reactants at equilibrium. Its numerical value may be obtained from the ratio of velocity constants, or, more usually and more easily, especially in complex reactions, by actual measurement of the concentrations present in the equilibrium mixture.

Equilibrium Constant for Some Familiar Reactions · Let us write the expression for the equilibrium constant for a few of the reactions referred to in the preceding pages of this book; and, as we do so, let us remember that coefficients are to appear as exponents of concentration.

For $2\,H_2 + O_2 \rightleftarrows 2\,H_2O$, we have $\dfrac{[H_2O]^2}{[H_2]^2 \times [O_2]} = K.$

For $N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$, we have $\dfrac{[NH_3]^2}{[N_2] \times [H_2]^3} = K.$

For $H_2 + I_2 \rightleftarrows 2\,HI$, we have $\dfrac{[HI]^2}{[H_2] \times [I_2]} = K.$

And for $H_3AsO_3 + I_2 + H_2O \rightleftarrows H_3AsO_4 + 2\,HI$, we have

$$\frac{[H_3AsO_4] \times [HI]^2}{[H_3AsO_3] \times [I_2] \times [H_2O]} = K.$$

To get the numerical values of K in these various equilibria we must, of course, know the concentrations of reactants and products at equilibrium. In the third reaction, for example, the equilibrium constant at 410° is obtained from the table on page 439 thus:

$$K = \frac{(0.01552)^2}{0.00224 \times 0.00224} = 48.$$

Regardless of the initial concentrations, the concentrations of reactants and products must satisfy the equilibrium constant above when equilib-

rium has been reached, provided the temperature remains constant. This is verified experimentally by the results in the table on page 441, where

$$K = \frac{(0.01865)^2}{0.010685 \times 0.000675} = 48.$$

At some temperature different from 410°, of course, the equilibrium constant will have a different value, since a given change in temperature will have an unequal effect on the rates of the two opposing reactions.

Active Mass of a Solid · A reaction taking place in a mixture of gases or in solution is said to be *homogeneous* because the concentration of each component is the same in every part of the mixture. This concentration can be stated in gram-molecular weights per liter. When a *solid* is acted upon by a gas, as in the reaction of steam upon iron, or by a liquid, as when hydrochloric acid acts upon zinc, the reaction is said to be *heterogeneous* because some of the components present do not mix with one another. When steam and hot iron react in a closed vessel, an equilibrium is established according to the equation

$$4\ H_2O + 3\ Fe \rightleftarrows Fe_3O_4 + 4\ H_2$$

We have no difficulty in defining the concentration of the steam and in seeing that every molecule of it is available for the reaction. With the iron the case is different. Only those atoms forming the surface of the solid, or given off as vapor, can have any effect upon the velocity of the reaction at a given time; and in either case the effect will be practically constant. *That portion of a substance which is available for a reaction at a given time is called its active mass,* and it is with the active mass that the law of mass action is concerned. The best we can do in regard to the active mass of a solid is to consider it as a constant during the reaction. If, in the equilibrium equation

$$\frac{[H_2]^4 \times [Fe_3O_4]}{[H_2O]^4 \times [Fe]^3} = K',$$

we consider $[Fe_3O_4]$ and $[Fe]$ as constants and incorporate them in K', we get

$$\frac{[H_2]^4}{[H_2O]^4} = K$$

as the equilibrium constant for this reaction.

Reactions of Dissociation · There is a type of chemical reaction, many examples of which are known, in which a solid decomposes, or *dissociates,* into a second solid and a gas. Thus the carbonates, when heated, yield an oxide of the metal and carbon dioxide:

$$CaCO_3 \rightleftarrows CaO + CO_2$$

We express the equilibrium constant for this reaction thus:

$$\frac{[CaO] \times [CO_2]}{[CaCO_3]} = K'$$

But both CaO and $CaCO_3$ are *solids*, and their active masses, or concentrations, may each be regarded as constant and may be designated by c' and c''. We shall then have

$$\frac{c' \times [CO_2]}{c''} = K', \quad \text{or} \quad [CO_2] = \frac{K' \times c''}{c'} = K$$

In other words, the concentration of CO_2 in equilibrium with CaO and $CaCO_3$ must be *constant* at a given temperature. But the concentration of a gas is proportional to its pressure: so we may say that at a given temperature the *pressure* of CO_2 in contact with CaO and $CaCO_3$ is *constant*. This constant pressure, due to the gas formed, is called the *dissociation pressure* of the solid from which the gas is formed.

Efflorescence of Hydrates · An entirely similar case is presented by many hydrated salts which tend to lose water (as vapor) and form a lower hydrate or an anhydrous salt, thus:

$$\underset{\text{solid}}{Na_2SO_4 \cdot 10\ H_2O} \rightleftarrows \underset{\text{solid}}{Na_2SO_4} + \underset{\text{vapor}}{10\ H_2O}$$

At a definite temperature the salt will give off water vapor until equilibrium is reached with the two solids concerned in the reaction. In the open air, where the water vapor can continuously escape, no equilibrium can be reached, *unless the partial pressure of the water vapor present in the air is equal to the dissociation pressure of the hydrate.* If this partial pressure is *equal to* (or greater than) the dissociation pressure of the hydrate, no dissociation occurs. If it is *less*, the hydrate steadily loses water vapor to the air, and usually crumbles to powder consisting of the anhydrous salt or a lower hydrate. Loss of water in this way is called *efflorescence*, and the hydrate is said to be *efflorescent* in air.

QUESTIONS

1. What is (*a*) *an equilibrium;* (*b*) *concentration;* (*c*) *catalysis;* (*d*) *Le Châtelier's principle;* (*e*) *an activated molecule;* (*f*) *the law of mass action;* (*g*) *a rate constant;* (*h*) *a reversible reaction;* (*i*) *an equilibrium constant;* (*j*) *the position of equilibrium;* (*k*) *dissociation pressure;* (*l*) *efflorescence?*

2. What is the reason for (*a*) storing eggs in *cold* storage; (*b*) using an *excess* of oxygen in the preparation of sulfuric acid by the contact process; (*c*) *heating* the water in which we want to dissolve something; (*d*) using a *pressure* above atmospheric in the Haber process; (*e*) using an electric *spark* in the Birkeland-Eyde process?

3. What effect does a catalyst have (*a*) on the speed of a reaction; (*b*) on the position of equilibrium?

4. Why should the concentrations used to calculate rate constants and equilibrium constants be expressed as gram-molecular weights rather than as grams?

5. (*a*) How do you explain the statement "At equilibrium, although no reaction seems to be taking place, actually both reactions continue, but at equal rates"? (*b*) Does this mean that the rate constants are equal? (*c*) How could this statement be verified experimentally?

6. The reaction $4\ HCl + O_2 \rightleftarrows 2\ H_2O + 2\ Cl_2$ takes place with the evolution of heat. What will be the effect (*a*) on the rate of the forward reaction, (*b*) on the rate of the reverse reaction, and (*c*) on the position of equilibrium if the following changes are made in a mixture of the four gases at equilibrium at 150° and 1 atm: (1) the pressure is raised to 1.5 atm; (2) the temperature is raised to 200°; (3) more steam is added to the equilibrium mixture; (4) the temperature is lowered to 140°; (5) a catalyst is introduced?

7. *a.* Write the expressions for the equilibrium constants for the following reactions:

(1) $2\ SO_2 + O_2 \rightleftarrows 2\ SO_3 + \text{heat}$
(2) $CO_2 + H_2 \rightleftarrows H_2O + CO + \text{heat}$
(3) $Na_2SO_4 \cdot 10\ H_2O \rightleftarrows Na_2SO_4 + 10\ H_2O - \text{heat}$
(4) $N_2 + O_2 \rightleftarrows 2\ NO - \text{heat}$
(5) $C + CO_2 + \text{heat} \rightleftarrows 2\ CO$

b. What would be the effect on (1) the equilibrium constants and (2) the position of equilibrium of doubling the pressure; of increasing the temperature?

8. What is the difference between a static and a dynamic equilibrium?

9. How do you explain the fact that many reactions take place very rapidly in solution which do not take place at all or only slowly when the solid substances are found together?

10. Given the equation $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$, how can you make the reaction move (*a*) toward the left; (*b*) toward the right?

11. State Le Châtelier's principle and illustrate it with the effect of increased pressure (*a*) on a chemical equilibrium; (*b*) on a melting point; (*c*) on a freezing point.

12. Explain the behavior of certain salt hydrates (*a*) in moist climates; (*b*) in dry climates.

13. To make ammonia according to the equation $N_2 + 3\ H_2 \longrightarrow 2\ NH_3$, the mixed gases are subjected to high pressure for a good yield. But the temperature is kept below 500°, in spite of the fact that at higher temperatures the velocity of the reactions would be greater. Explain.

14. If a solute is more soluble in a hot solvent than in a cold solvent, is the solution process (*a*) exothermic or (*b*) endothermic?

PROBLEMS

1. If a certain chemical reaction proceeds at such a rate as to form about 1 g of product per hour at 30°, about how many grams per hour would be formed at 100°?

2. If the concentrations of A, B, C, and D at equilibrium in the reaction represented by

$$A + B \rightleftarrows C + D$$

are respectively 0.300, 0.400, 0.500, and 0.600 molar, calculate (*a*) the numerical value of the equilibrium constant; (*b*) the concentration of D when the concentrations of A, B, and C are respectively 0.300, 0.400, and 1.000 molar; (*c*) the concentrations of C and D when 0.300 g-mol. wt of A and 0.300 g-mol. wt of B are mixed in a 1-liter volume and the system allowed to come to equilibrium.

3. Calculate the rate of the reaction $H_2 + I_2 \longrightarrow 2\ HI$ at 410° when the concentration of hydrogen is 0.01 molar and the concentration of iodine is 0.05 molar.

4. Calculate the concentration of the hydrogen iodide formed when hydrogen and iodine, each at a concentration of 0.02 molar, are mixed and allowed to come to equilibrium at 410°.

5. The total reaction $2\ A + B \longrightarrow 3\ C + D$ is found to proceed through the steps $A + B \longrightarrow Q + C$; $Q + A \longrightarrow R + D$; $R \longrightarrow 2\ C$. The first step is rate-determining. (*a*) Give the mathematical equation which expresses the rate of the total reaction. (*b*) Give the equation for the equilibrium constant of the total reaction. (*c*) Write the expressions for the law of mass action for the forward and reverse reactions for each of the steps, and show that, when all three steps come to equilibrium, the product of the equilibrium constants for the three steps is equal to the equilibrium constant of the total reaction. (*d*) Make general statements relating the equilibrium constant of a total reaction, which takes place in steps, to the rate constants and equilibrium constants of the individual steps.

CHAPTER 25

EQUILIBRIUM IN IONIC SOLUTIONS

Ionic Equilibrium · Reactions involving electrolytes are so fast that we have difficulty in measuring their rates. Such reactions are, however, commonly reversible and come almost instantaneously to an equilibrium; it is often easy to determine the position of equilibrium, even though it is not easy to measure the rate of the forward or reverse reaction. These ionic equilibria obey the usual laws relating to equilibrium; one may set up equilibrium constants involving concentrations of reactants and products, and Le Châtelier's principle (Chap. 24) applies to them. The latter is particularly useful in suggesting the conditions under which reactions go to completion.

Completion of Reactions · Discussion in Chapter 24 indicates that reversible reactions between ions do not go to completion. What we mean when we say that a reaction is complete is that the position of equilibrium has been displaced so far toward the products that all but an insignificant quantity of one or more of the reactants has been used up in the reaction. Le Châtelier's principle tells us immediately how the position of equilibrium can be displaced in this fashion. Ionic reactions will go largely to completion if any one of the following conditions obtains:

1. **The driving force of the reaction is sufficiently great.** Some ionic reactions involve the transfer of electrons, and hence oxidation and reduction take place. In many of these the tendency of one of the reactants to acquire electrons is so much greater than the tendency of the other to retain them that the second reactant is changed almost completely into its oxidized form. For example, if a solution of bromine is added to a solution containing the stannous ion (Sn^{++}), the bromine acquires electrons from the stannous ion, oxidizing it to the stannic ion (Sn^{++++}):

$$Br_2 + Sn^{++} \longrightarrow Sn^{++++} + 2\,Br^- \qquad (1)$$

The stannous ion is unable to retain its electrons in the presence of bromine, and the reaction goes practically to completion.

2. **A large excess of one of the reactants is added.** This displaces the equilibrium to such an extent that the other reactant is almost all used up in forming the reaction products, so that with respect to that reactant the reaction is complete. The operation of this rule is, of course, not restricted to ionic equilibria. (See Chapter 24.)

3. **The reaction is such that the formation of the product removes ions from the solution.** If any of the ions produced in a reaction are removed from the solution, they cannot take part in the reverse reaction. Of course the ions are never completely removed, but their concentrations are so low that the concentrations of the reacting ions are also very low when equilibrium is established; hence we say that the reaction has gone to completion. In addition to removal by oxidation-reduction processes ions may be removed in three general ways.

a. By the formation of a compound which is but slightly ionized. This is the reaction which takes place when, for example, a strong acid and a strong base neutralize each other, with the removal of hydrogen ions and hydroxyl ions to form water:

$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow H_2O + Na^+ + Cl^- \qquad (2)$$

Such reactions are complete.

b. By the formation of a solid which is but slightly soluble and which precipitates out. This occurs when, for example, silver nitrate and sodium chloride solutions are mixed, with the formation of insoluble silver chloride (p. 214). This removes silver and chloride ions and sends the reaction to completion:

$$Ag^+ + NO_3^- + Na^+ + Cl^- \longrightarrow AgCl\downarrow + Na^+ + NO_3^- \qquad (3)$$

c. By the formation of a gas which is but slightly soluble under the conditions used. The reaction between concentrated sulfuric acid and sodium chloride is complete because the hydrogen chloride formed passes off as a gas, with the removal of hydrogen and chloride ions:

$$Na^+ + Cl^- + H^+ + HSO_4^- \longrightarrow Na^+ + HSO_4^- + HCl\uparrow \qquad (4)$$

Such qualitative statements about the completion of reactions, while important, are not as valuable as the results obtained by a quantitative application of the equilibrium principle to ionic reactions. Some of these applications are discussed in the following sections.

Ionization of Weak Acids · A solution of a weak acid contains both molecules and ions (p. 212), the ionization being a reversible reaction:

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^- \qquad (5)$$

If the reaction is reversible, it must reach an equilibrium. The concentrations at equilibrium must agree with the terms of the equilibrium constant, written as the product of the molar concentrations of the reaction products (for the reaction above, hydrogen ions and acetate ions) divided by the molar concentration of the reactant (acetic acid). Since

this represents an ionization equilibrium, the equilibrium constant is called an *ionization constant*, and is written K_{ion}:

$$K = K_{ion} = \frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]}. \quad (6)$$

A weak dibasic acid, which ionizes in two steps, will have two ionization constants. For example, hydrogen sulfide ionizes thus:

$$H_2S \rightleftarrows H^+ + HS^- \quad (7)$$

$$HS^- \rightleftarrows H^+ + S^{--} \quad (8)$$

and has the two ionization constants

$$K'_{ion} = \frac{[H^+] \times [HS^-]}{[H_2S]}, \quad (9)$$

$$K''_{ion} = \frac{[H^+] \times [S^{--}]}{[HS^-]}. \quad (10)$$

The numerical values of these constants must be experimentally determined, as usual, by measuring the concentrations of the substances involved when equilibrium is established. The value for the second ionization constant is commonly much smaller than that for the first. The values for a few common weak acids are given in the table on page 454.

Example 1. In a solution made by dissolving 0.1 g-mol. wt of acetic acid in enough water to make 1 liter of solution, the hydrogen ion concentration was found to be 0.00134 molar. Calculate the ionization constant of acetic acid.

By the chemical equation (5) one acetate ion is formed for each hydrogen ion when acetic acid ionizes. Consequently the acetate ion concentration is equal to the hydrogen ion concentration:

$$[H^+] = [C_2H_3O_2^-] = 0.00134.$$

Similarly one acetic acid molecule disappears for each hydrogen (or acetate) ion formed, and the concentration of acetic acid is equal to the difference between the amount originally present and the amount which ionizes:

$$[HC_2H_3O_2] = 0.1 - 0.00134 = 0.09866.$$

Substituting these values for the concentrations in the expression for the ionization constant (equation (6)), we may calculate the numerical value of K_{ion} thus:

$$K_{ion} = \frac{0.00134 \times 0.00134}{0.09866} = 1.82 \times 10^{-5}.$$

Common-Ion Effect · Since the ionization of a weak acid involves an equilibrium, any change in the concentration of one of the substances present must change the position of the equilibrium, by Le Châtelier's principle. If, for example, we add acetate ions to a solution of acetic

acid, the position of the equilibrium in reaction (5) must shift toward the left to relieve the stress of the increased acetate ion concentration. A shift to the left can occur only by the reaction of acetate ions with hydrogen ions already present in the solution; this reaction reduces the concentration of hydrogen ions. The observed result is thus a decrease in the acidity of the solution, due to the shift in the position of equilibrium when acetate ions are added to an acetic acid solution. (Of course we cannot add a solution containing acetate ions alone; some positive ions must also be present. Sodium acetate solution, for example, will contain sodium ions and acetate ions, since sodium acetate, being a salt and a strong electrolyte, is completely ionized.) Such a displacement of the position of an ionic equilibrium, due to the addition of an ion involved in the equilibrium, is called the *common-ion effect.*

Example 2. In Example 1 the value of the ionization constant for acetic acid was found to be 1.82×10^{-5}. Calculate the $[H^+]$ in a 0.1 molar solution of acetic acid in which the $[C_2H_3O_2^-]$ has been increased to 0.2 molar by adding sodium acetate.

Let $[H^+] = x;$

further, $[C_2H_3O_2^-] = 0.2,$

and $[HC_2H_3O_2] = 0.1 - x.$

Substituting these values in the formula for the ionization constant for acetic acid, we have

$$K_{\text{ion}} = \frac{x \times 0.2}{0.1 - x} = 1.82 \times 10^{-5}.$$

This equation may be easily solved for x. However, the calculation may be simplified by observing that even in Example 1 the hydrogen ion concentration was only 0.00134 molar, and that, by the common-ion effect, it will be even less in the present case. Consequently, since x is small, $0.1 - x$ is nearly equal to 0.1, and we may substitute 0.1 for $0.1 - x$:

$$K_{\text{ion}} = \frac{x \times 0.2}{0.1 - x} = \frac{x \times 0.2}{0.1} = 1.82 \times 10^{-5},$$

whence $x = 0.91 \times 10^{-5} = 0.0000091$ molar.

If this value of the hydrogen ion concentration is compared with its value in the absence of the added acetate ion (Example 1), it can be seen that the common-ion effect has resulted in decreasing the hydrogen ion concentration more than a hundredfold.

Ionization of Weak Bases · What has been said above about the ionization of weak acids can be applied directly to the ionization of weak

IONIZATION CONSTANTS OF WEAK ACIDS AND A WEAK BASE

COMPOUND	IONIZATION EQUATION	K_{ion} FOR ACIDS AND BASE AT ROOM TEMPERATURE
Acids		
Acetic	$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$	$K_{ion} = \frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$
Carbonic	$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$	$K'_{ion} = \frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = 3 \times 10^{-7}$
	$HCO_3^- \rightleftarrows H^+ + CO_3^{--}$	$K''_{ion} = \frac{[H^+] \times [CO_3^{--}]}{[HCO_3^-]} = 6 \times 10^{-11}$
Hydrosulfuric	$H_2S \rightleftarrows H^+ + HS^-$	$K'_{ion} = \frac{[H^+] \times [HS^-]}{[H_2S]} = 9 \times 10^{-8}$
	$HS^- \rightleftarrows H^+ + S^{--}$	$K''_{ion} = \frac{[H^+] \times [S^{--}]}{[HS^-]} = 1 \times 10^{-15}$
Hydrocyanic	$HCN \rightleftarrows H^+ + CN^-$	$K_{ion} = \frac{[H^+] \times [CN^-]}{[HCN]} = 7 \times 10^{-10}$
Phosphoric	$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$	$K'_{ion} = \frac{[H^+] \times [H_2PO_4^-]}{[H_3PO_4]} = 1 \times 10^{-2}$
	$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{--}$	$K''_{ion} = \frac{[H^+] \times [HPO_4^{--}]}{[H_2PO_4^-]} = 6 \times 10^{-8}$
	$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---}$	$K'''_{ion} = \frac{[H^+] \times [PO_4^{---}]}{[HPO_4^{--}]} = 5 \times 10^{-13}$
Base		
Ammonium hydroxide	$NH_4OH \rightleftarrows NH_4^+ + OH^-$	$K_{ion} = \frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}$

bases. The weak base ammonium hydroxide, for example, ionizes to form ammonium and hydroxyl ions:

$$NH_4OH \rightleftarrows NH_4^+ + OH^- \tag{11}$$

Its ionization constant is written

$$K_{ion} = \frac{[NH_4^+] \times [OH^-]}{[NH_4OH]}. \tag{12}$$

The addition of ammonium chloride to the solution will displace the position of the equilibrium to the left, since the ammonium ion is common to both ammonium chloride and ammonium hydroxide solutions.

Ion Equilibrium for Water · Although for many purposes water may be considered an un-ionized compound, in other cases account must be taken of its slight dissociation, according to the equation

$$H_2O \rightleftarrows H^+ + OH^- \tag{13}$$

The equilibrium constant for this reaction is

$$K = \frac{[H^+] \times [OH^-]}{[H_2O]}, \tag{14}$$

and the concentrations of hydrogen and hydroxyl ions must conform to this expression not only in pure water, but in any solution containing water. In the dilute solutions commonly used in the laboratory the concentration of undissociated water does not change noticeably with changes in the concentrations of other substances present, and the numerical value of $[H_2O]$ may be set equal to the constant value 55.5 molar. (One liter of water contains 1000 g of H_2O, or $\frac{1000}{18} = 55.5$ g-mol. wt.) Multiplying this value by the equilibrium constant, we obtain a new constant, called the *ion-product constant* for water, K_w:

$$K_w = 55.5 \times K = [H^+] \times [OH^-]. \tag{15}$$

Exact measurements have shown that in pure water the numerical value of $[H^+] = 1 \times 10^{-7}$ molar; this must also be the concentration of OH^-, since, by the chemical equation (13), one hydroxyl ion is formed each time one hydrogen ion is formed. Substituting these values we find the numerical value of K_w:

$$K_w = 1 \times 10^{-7} \times 1 \times 10^{-7} = 1 \times 10^{-14}. \tag{16}$$

If we add an acid to the neutral water, $[H^+]$ increases and $[OH^-]$ decreases; if we add a base, $[OH^-]$ increases and $[H^+]$ must diminish. But their product, $[H^+] \times [OH^-]$, still keeps the constant value 10^{-14}, regardless of other ions added to the water.

p*H *Value · Very slight changes in acidity and alkalinity are frequently of great significance, and the values of small concentrations of hydrogen

or hydroxyl ions have to be written and referred to very often. It has become customary to indicate these by merely stating the value of the *exponent* of the molar concentration (omitting the minus sign). This value of the hydrogen ion concentration is designated by the symbol *p*H. Thus, we say that the *p*H value for water is 7, meaning that in 1 liter of water the concentration of the H^+ ion (and also that of the OH^- ion) is 1×10^{-7} $\vec{M}$. Using this method of representation we may construct the following table:

RELATION OF *p*H VALUE TO H^+ AND OH^- CONCENTRATIONS

MOLAR CONCENTRATION OF H+		*p*H	MOLAR CONCENTRATION OF OH^-
1	10^0	0	10^{-14}
0.1	10^{-1}	1	10^{-13}
0.01	10^{-2}	2	10^{-12}
0.0001	10^{-4}	4	10^{-10}
0.0000001	10^{-7}	7	10^{-7} (neutral water)
0.0000000001	10^{-10}	10	10^{-4}
Etc.	Etc.	Etc.	Etc.

Thus, as the acidity *decreases*, the *p*H value (by definition) *increases*. A solution of *p*H value greater than 7 is basic or *alkaline*.

Example 3. What is the *p*H of a solution 0.001 molar in sodium hydroxide?

Since $[OH^-] = 0.001 = 10^{-3}$,
and $K_w = [H^+] \times [OH^-] = 10^{-14}$,
then $[H^+] \times 10^{-3} = 10^{-14}$,
and $[H^+] = 10^{-11}$,
or $pH = 11$.

Buffer Solutions · Many chemical reactions must be carried out at a constant and controlled *p*H. A solution of *p*H 5 can be prepared by making the solution 1×10^{-5} molar in hydrochloric acid, but it cannot readily be maintained at that figure, since the accidental entrance of the smallest amount of base will neutralize some of the acid and raise the *p*H, while a small amount of acid will lower the *p*H. This difficulty is avoided by using a *buffer solution*, containing a weak acid and a salt of that acid — for example, acetic acid and sodium acetate. This solution contains in it large reservoirs of acetic acid molecules and of acetate ions from the sodium acetate. If a small amount of base is added to the solution, it is true that some of the hydrogen ions are removed to form water, but more of the acetic acid molecules then dissociate, to re-establish an equilibrium concentration of hydrogen ions only negligibly different from the original concentration. The position of equilibrium in the reaction

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^- \qquad (17)$$

shifts slightly to the right to compensate for the hydrogen ions removed by the base. The addition of a small amount of acid simply causes the hydrogen ions of the added acid to react with the acetate ions from the sodium acetate, so that again the $[H^+]$ does not change. The solution is thus protected, or *buffered*, against a change in $[H^+]$ on the addition of either acid or base, and maintains a nearly constant *p*H, regardless of the addition of these substances. Buffer solutions containing weak bases and their salts can also be used.

Human blood is buffered at a *p*H of 7.2; that is, the hydrogen ion concentration is between 10^{-7} and 10^{-8} molar. It is maintained at this value by buffer mixtures, such as the weak acid carbonic acid and its salt sodium bicarbonate ($NaHCO_3$). If for any reason, the *p*H of the blood varies from 7.2 by a significant amount, serious consequences, even death, inevitably follow.

Hydrolysis · If a salt of a strong base and a weak acid, such as sodium acetate, is added to water, the anions of the acid tend to react with the hydrogen ions of the water to form undissociated molecules of the acid:

$$C_2H_3O_2^- + H^+ \longrightarrow HC_2H_3O_2 \tag{18}$$

There is thus a competition between the hydroxyl ions and the acetate ions for the hydrogen ions present, as is indicated by the equations

$$OH^- + H^+ \longrightarrow H_2O \tag{19}$$

$$C_2H_3O_2^- + H^+ \longrightarrow HC_2H_3O_2 \tag{20}$$

If the ionization constant of the acid is small enough, an appreciable number of the hydrogen ions may be removed to form undissociated acid. The ion product $[H^+] \times [OH^-]$ must always equal 10^{-14}, so that if $[H^+]$ is diminished, $[OH^-]$ must increase by the ionization of water: $H_2O \longrightarrow H^+ + OH^-$. The result of this increase in the hydroxyl ion concentration is that the solution becomes alkaline, as can be observed experimentally by testing with an indicator. Such a reaction of the ions of a salt with the ions of water is called a *hydrolysis reaction.*

Following the usual convention of writing slightly ionized substances as molecules, we may show what happens in a hydrolysis reaction by writing

$$\begin{array}{rcl} & Na^+ + C_2H_3O_2^- & \\ & + & \\ H_2O \rightleftarrows OH^- + & H^+ & \\ & \downarrow\uparrow & \\ & HC_2H_3O_2 & \end{array} \tag{21}$$

That the solution becomes alkaline depends upon the fact that the sodium and hydroxyl ions have no tendency to form an *undissociated* sodium hydroxide molecule, since sodium hydroxide is a strong base. The hydroxyl ions are therefore left free, while the hydrogen ions are removed to form undissociated molecules.

The same reaction may be expressed in a single equation:

$$C_2H_3O_2^- + H_2O \rightleftarrows HC_2H_3O_2 + OH^- \tag{22}$$

since the sodium ions play no part in the reaction. The equilibrium constant for this reaction is

$$K = \frac{[HC_2H_2O_3] \times [OH^-]}{[C_2H_3O_2^-] \times [H_2O]}. \tag{23}$$

Since, as indicated above, the numerical value of $[H_2O]$ is constant and equal to 55.5 molar, it is convenient to multiply through by that figure to obtain the *hydrolysis constant*:

$$K_h = 55.5\ K = \frac{[HC_2H_3O_2] \times [OH^-]}{[C_2H_3O_2^-]}. \tag{24}$$

If the ionic equation (22) is written as a molecular equation,

$$NaC_2H_3O_2 + H_2O \rightleftarrows HC_2H_3O_2 + NaOH \tag{25}$$

it is seen that *the hydrolysis reaction is the reverse of a neutralization reaction.* This statement is sometimes used as a definition of hydrolysis.

The hydrolysis of a salt of a weak base and a strong acid results in a solution which is acid, since the cations of the weak base remove hydroxyl ions to form undissociated molecules of the base. This leaves hydrogen ions in excess, since these do not combine with the anions of the strong acid. With ammonium chloride as an example, the equation for the reaction is

$$NH_4^+ + Cl^- + H_2O \rightleftarrows NH_4OH + H^+ + Cl^- \tag{26}$$

or

$$NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+ \tag{27}$$

and the hydrolysis constant is

$$K_h = \frac{[NH_4OH] \times [H^+]}{[NH_4^+]}. \tag{28}$$

The hydrolysis of a salt of a weak base and a weak acid is likely to be very great, since both the hydrogen and the hydroxyl ions form undissociated molecules with the ions of the salt. Thus, with ammonium acetate, the equation for the reaction is

$$NH_4^+ + C_2H_3O_2^- + H_2O \rightleftarrows NH_4OH + HC_2H_3O_2 \tag{29}$$

A salt of a strong base and a strong acid does not hydrolyze. It is evident from the discussions above that when salts of this class are dissolved in water, neither the hydrogen nor the hydroxyl ions are withdrawn in appreciable amounts; hence their solutions are approximately neutral.

The Action of Water upon Acid Salts · The acid salts of *strong* acids readily ionize in aqueous solutions, yielding hydrogen ions. Thus, sodium hydrogen sulfate ionizes as follows:

$$NaHSO_4 \rightleftarrows Na^+ + HSO_4^- \quad (30)$$

$$HSO_4^- \rightleftarrows H^+ + SO_4^{--} \quad (31)$$

In dilute solutions both the reactions expressed in equations (30) and (31) are practically complete. Such solutions, therefore, have an acid reaction, due to the hydrogen ions. The case is different, however, with acid salts of *weak* acids, since the hydrogen present in such salts is not ionized to any appreciable extent when the salts are dissolved in water. Sodium hydrogen sulfide, for example, ionizes as follows:

$$NaHS \rightleftarrows Na^+ + HS^- \quad (32)$$

$$HS^- \rightleftarrows H^+ + S^{--} \quad (33)$$

The reaction indicated in equation (33), however, takes place only to a very slight extent. A solution like this will therefore contain such a comparatively small number of hydrogen ions that it will have either a neutral or, at most, only a slightly acid reaction. Indeed, in the case of an acid salt derived from a strong base and a very weak acid, hydrolysis may take place to such an extent that its solution becomes basic. For example, sodium hydrogen carbonate ($NaHCO_3$), an acid salt of carbonic acid (H_2CO_3), dissolves in water, forming the ions Na^+ and HCO_3^-. Since carbonic acid is a very weak acid, scarcely ionizing at all in solution, it will be formed by the union of the ions HCO_3^- with the hydrogen ions of the water:

$$H^+ + HCO_3^- \rightleftarrows H_2CO_3 \quad (34)$$

This withdrawal of the hydrogen ions from the water results in the accumulation of the accompanying hydroxyl ions to such an extent that the solution becomes basic in reaction.

Saturation Equilibria Involving Electrolytes · We have seen, in Chapter 12, that in a saturated solution in contact with an undissolved solid solute, an equilibrium exists between the dissolved and the undissolved solute. If the solute is a strong electrolyte, then it exists in solution as ions only; the reaction of dissolving barium sulfate, for example, is expressed by the equation

$$BaSO_4 \rightleftarrows Ba^{++} + SO_4^{--} \quad (35)$$

For this reaction we may write an equilibrium constant in the usual manner; it is

$$K = \frac{[Ba^{++}] \times [SO_4^{--}]}{C_{BaSO_4}}, \tag{36}$$

where C_{BaSO_4} is used to indicate that the barium sulfate is a solid and therefore of constant concentration. Multiplying this by the equilibrium constant (pp. 447, 455) we obtain a new constant, called the *solubility-product constant*, K_{sp}:

$$K_{sp} = K \times C_{BaSO_4} = [Ba^{++}] \times [SO_4^{--}]. \tag{37}$$

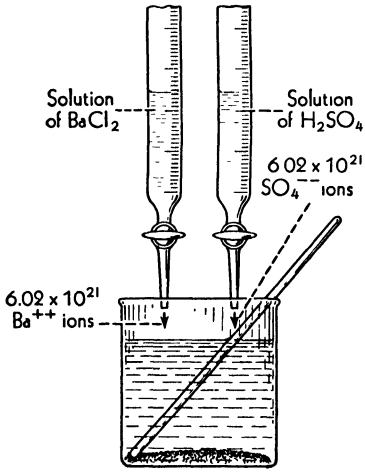


Fig. 25-1. Precipitation of Barium Sulfate

The numerical value of the solubility-product constant is determined experimentally by measuring the concentrations in a saturated solution; for barium sulfate at 18° it is 1×10^{-10}. In any saturated solution of barium sulfate the product of the concentrations of barium and sulfate ions is equal to 1×10^{-10}. If, when solutions of barium and sulfate ions are mixed, the product of their concentrations is greater than 1×10^{-10}, then barium sulfate will precipitate out as a solid until the concentrations are reduced to such an extent that their product equals K_{sp}. If, when solutions of the two ions are mixed, the product of their concentrations is less than 1×10^{-10}, nothing happens; we then have an unsaturated solution, and the ion product can have any value so long as it does not reach K_{sp}, which applies only to saturated solutions.

Solubility and the Common-Ion Effect · Suppose that barium chloride and sulfuric acid solutions containing exactly equivalent amounts, say 0.01 mole of each substance, are mixed (Fig. 25-1). Barium sulfate will precipitate as a result of the reaction

$$Ba^{++} + SO_4^{--} \rightleftarrows BaSO_4\downarrow \tag{38}$$

Then, after the precipitate has settled, a further slight precipitation from the saturated solution can be obtained by adding an excess of either Ba^{++} or SO_4^{--}. This is predicted by Le Châtelier's principle, since increasing the concentration of one of the substances on the left of equation (38) will shift the position of equilibrium to the right. The amount

by which the equilibrium will shift can be calculated from the solubility-product constant and the amount of excess ion added, since an increase in $[Ba^{++}]$, for example, must be compensated for by a decrease in $[SO_4^{--}]$ if K_{sp} is to remain constant. The only possibility for decreasing $[SO_4^{--}]$ is for sulfate ions to react with barium ions to precipitate barium sulfate (equation (38)). The use of an excess of one of the precipitating ions to remove all but a negligible quantity of the other from the solution is a common laboratory practice; it is another example of the application of the *common-ion effect.*

Example 4. Calculate the molar concentration of the sulfate ion in a saturated solution of barium sulfate.

The K_{sp} for barium sulfate is 1×10^{-10}, or

$$[Ba^{++}] \times [SO_4^{--}] = 1 \times 10^{-10}.$$

Let $[SO_4^{--}] = x$. By the chemical equation (38) the molar concentration of the sulfate ion must equal the molar concentration of the barium ion when only barium sulfate is present; so $[Ba^{++}] = [SO_4^{--}] = x$. Substituting in the expression for the solubility-product constant, we get

$$x \times x = 1 \times 10^{-10};$$

therefore $x = 1 \times 10^{-5}$, or 0.00001 g-ionic wt of Ba^{++} or SO_4^{--} per liter.

Example 5. Calculate the concentration of the sulfate ion in a saturated solution of barium sulfate to which barium chloride is added until $[Ba^{++}] = 0.1\ M$.

Let $[SO_4^{--}] = x$. In this case $[Ba^{++}]$ is no longer equal to $[SO_4^{--}]$, since additional barium ion is present; in fact, according to the problem, $[Ba^{++}] = 0.1$ molar. Substituting in the expression for K_{sp},

$$[Ba^{++}] \times [SO_4^{--}] = 1 \times 10^{-10},$$

we get

$$0.1 \times x = 1 \times 10^{-10};$$

therefore $x = 1 \times 10^{-9}$, or 0.000000001 g-ionic wt of SO_4^{--} per liter.

Thus, the addition of more barium ion has decreased the sulfate ion concentration from 0.00001 molar (Example 4) to 0.000000001 molar, as predicted by the common-ion effect.

Precipitation of Insoluble Salts · When several ions are mixed in a solution, a salt will precipitate when the value of its solubility-product constant would be exceeded if it did not precipitate. Thus, when sodium chloride and silver nitrate solutions are mixed (p. 451), four compounds might result from the ions in solution—namely, sodium chloride, sodium nitrate, silver nitrate, and silver chloride. Of these four the silver chloride has by far the smallest solubility-product constant, and it is the one that precipitates out until the concentrations of the silver ion and the chloride ion have been reduced sufficiently to satisfy the expression

$$K_{sp} = [Ag^+] \times [Cl^-]. \qquad (39)$$

Dissolving Insoluble Salts · If one adds nitric acid to silver chloride, the silver chloride does not dissolve. But if one adds nitric acid to silver acetate, which is also insoluble, solution occurs. The difference is that silver chloride is a salt of the *strong* acid HCl, while silver acetate is the salt of the *weak* acid $HC_2H_3O_2$. When an acid is added to silver acetate, the hydrogen ions combine with the acetate ions to form undissociated acetic acid. This reduces the concentration of acetate ions, and by Le Châtelier's principle the solubility equilibrium shifts so as to introduce more acetate ions into the solution. These react immediately with hydrogen ions to form acetic acid, so that the solubility-product constant is not maintained and all the silver acetate dissolves. The direction of the shift of equilibria is represented by the heavy arrows below.

$$\underset{\text{solid}}{AgC_2H_3O_2} \rightleftharpoons Ag^+ + C_2H_3O_2^- \qquad (40)$$
$$+$$
$$H^+$$
$$\downarrow\uparrow$$
$$HC_2H_3O_2$$

The solution finally contains acetic acid and the ions of silver nitrate (and those of excess nitric acid). No undissociated molecules, such as $HC_2H_3O_2$, can form with silver chloride; so silver chloride does not dissolve in nitric acid. In general, the insoluble salt of a strong acid is insoluble in acids, as well as in water, while the insoluble salt of a weak acid will dissolve in a strong acid.

Conversely, one cannot precipitate silver acetate by adding acetic acid to silver nitrate, since the concentration of the acetate ion in acetic acid solutions is not great enough to cause the solubility-product constant of silver acetate to be exceeded. On the other hand, silver chloride precipitates immediately when hydrochloric acid is added to silver nitrate.

Complex Ions · Silver chloride will dissolve in ammonium hydroxide solutions, owing to the formation of the *complex ion* $Ag(NH_3)_2^+$. This ion is formed by the addition of two neutral ammonia molecules, always present in ammonium hydroxide solutions, to a silver ion. This reduces the concentration of the simple silver ion (Ag^+) and causes the solubility equilibrium to shift in an attempt to re-establish the solubility-product constant, the equilibria shifting as indicated by the heavy arrows:

$$\underset{\text{solid}}{AgCl} \rightleftharpoons Ag^+ + Cl^- \qquad (41)$$
$$+$$
$$2\,NH_3$$
$$\downarrow\uparrow$$
$$Ag(NH_3)_2^+$$

Complex ions of ammonia are common with many metals. As indicated, they are in equilibrium with the simple ion and ammonia, and have *association constants* such as that of the silver ammonia complex ion:

$$K = \frac{[Ag(NH_3)_2^+]}{[Ag^+] \times [NH_3]^2}. \tag{42}$$

QUESTIONS

1. Tell what is meant by (*a*) *driving force of a reaction;* (*b*) *stepwise ionization;* (*c*) *ionization constant;* (*d*) *common-ion effect;* (*e*) *hydrolysis;* (*f*) *solubility-product constant;* (*g*) *mass action;* (*h*) *driving reactions to completion;* (*i*) *weak acid;* (*j*) *buffer solution;* (*k*) *pH value;* (*l*) *ion-product constant of water;* (*m*) *saturation equilibrium;* (*n*) *complex ion;* (*o*) *hydrolysis constant;* (*p*) *association constant.*

2. (*a*) Enumerate the conditions which tend to drive a reaction to completion. (*b*) Indicate which of those conditions exist in the following reactions: (1) the reaction of zinc with dilute sulfuric acid; (2) the reaction of sodium acid carbonate ($NaHCO_3$) with hydrochloric acid; (3) the reaction of calcium hydroxide with nitric acid; (4) the reaction of ammonium hydroxide with silver chloride; (5) the reaction of sulfuric acid with barium peroxide; (6) the preparation of chlorine with manganese dioxide; (7) the preparation of hydrogen chloride by the action of concentrated sulfuric acid on a chloride; (8) the decomposition of potassium chlorate by heat.

3. In terms of ionic equilibria explain why (*a*) a water solution of an acid salt like sodium acid sulfate ($NaHSO_4$) is acidic but a water solution of an acid salt like sodium acid carbonate ($NaHCO_3$) is basic; (*b*) lime "sweetens" soil; (*c*) aluminum sulfate will make soil acidic; (*d*) aluminum sulfide when added to water forms aluminum hydroxide and hydrogen sulfide; (*e*) the concentration of the hydrogen ions of the blood stream can be kept constant by the use of buffers; (*f*) salts of strong acids and strong bases do not hydrolyze; (*g*) the hydrogen ion concentration may be reduced by neutralization or by adding a salt of a strong base and a weak acid.

4. Why is the use of ionization constants limited to weak acids and weak bases?

5. (*a*) Write the expression for the solubility-product constant of (1) AgCl; (2) $PbCl_2$; (3) CuS; (4) Ag_2S; (5) $CaCO_3$; (6) $Ca_3(PO_4)_2$. (*b*) What is the relationship between the solubility of a compound and the value of its solubility-product constant? (*c*) What ions can be added to solutions containing the compounds listed in *a* which, in each case, will lower the concentration of the cation? Explain why.

6. Answer parts *a*, *b*, and *c* of Problem 11 in Chapter 41.

7. Hydrocyanic acid (HCN) is a weak acid which ionizes as follows:

$$HCN \rightleftarrows H^+ + CN^-$$

Potassium cyanide (KCN) is present in solution as potassium ions (K^+) and cyanide ions (CN^-). (*a*) If a gram-formula weight of potassium cyanide is dissolved in a solution of hydrogen cyanide which has a hydrogen ion concentration of 0.00001 (in gram-ionic weights per liter), what will happen to the concentration of hydrogen ions? (*b*) Explain.

8. Given the reaction $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$, how many ways can you think of for forcing the reaction (*a*) to the right? (*b*) to the left? (*c*) Under what conditions might it go to completion in either direction?

9. A saturated solution of hydrogen sulfide in water is used extensively in qualitative analysis, and the concentration of sulfide ions is controlled, within limits, by the addition of hydrochloric acid on the one hand and ammonium hydroxide on the other. (*a*) What effect would each of these reagents have on the $[S^{--}]$? (*b*) Explain your answer in terms of ionic equilibrium and the ionization constant.

10. In bleaching cloth or wood pulp with hypochlorite solutions, it is important that the *p*H should not drop below about 8, since at a *p*H of 7 the material is greatly weakened by chemical action. On the other hand, bleaching is very slow at a high *p*H. Suggest a method of controlling the *p*H.

11. Does (*a*) the salt of a weak acid and a strong base, (*b*) the salt of a strong acid and a weak base, (*c*) the salt of a strong acid and a strong base, produce an acidic, basic, or neutral solution?

12. Show that the hydrolysis constant for a salt of a strong base and a weak acid is equal to the ion-product constant for water divided by the ionization constant for the acid.

13. If to a 0.1 molar solution of HCN is added an equal volume of a 0.1 molar solution of NaOH, the $[H^+]$ concentration of the resulting solution is not 10^{-7} molar but 10^{-11} molar. Explain.

14. Write the ionic equation for the reaction representing the hydrolysis of each of the following salts: (*a*) ammonium chloride (NH_4Cl); (*b*) sodium acetate ($NaC_2H_3O_2$); (*c*) sodium phosphate (Na_3PO_4); (*d*) potassium cyanide (KCN).

PROBLEMS

1. Calculate the *p*H of a 0.01 molar solution of HNO_3, assuming complete ionization.

2. What is the concentration of acetate ion, $[C_2H_3O_2^-]$, in a solution which contains 1.8 g of acetic acid per liter, the acid being 2.45 per cent ionized?

3. A 0.1 molar solution of ammonium hydroxide contains 0.00134 mole of ammonium and hydroxyl ions per liter, and a 0.01 molar solution contains 0.00041 mole of these ions per liter. (*a*) Calculate the value of the ionization constant in each case. (*b*) The results should be the same. Why?

4. (*a*) Calculate the $[OH^-]$ of a 0.1 molar solution of ammonium hydroxide to which has been added enough ammonium chloride to make the ammonium ion concentration 0.2 molar. (*b*) Compare your answer with the data of Problem 3. Why should there be such a difference between the two results?

5. One liter of water, saturated with H_2S, can be shown by experiment to contain 0.95×10^{-4} g-ionic wt of H^+; 0.95×10^{-4} g-ionic wt of HS^-; 1.2×10^{-15} g-ionic wt of S^{--}; 0.1 g-mol. wt of H_2S. Calculate K' and K''.

6. The solubility of $BaCO_3$ is 0.018 g/liter. (*a*) What is the molar concentration of this solution? (*b*) Express this in exponential form. (*c*) If the compound is completely ionized, what is the solubility-product constant for $BaCO_3$?

7. The solubility of each of the following salts is given in terms of grams per 100 ml of solution. Calculate the solubility-product constant for each substance.

SUBSTANCE	SOLUBILITY
a. AgBr	1.65×10^{-5}
b. AgI	2.88×10^{-7}
c. Ag_2CrO_4	4.32×10^{-3}
d. SrF_2	1.22×10^{-2}

8. The solubility-product constants are given below for a few difficultly soluble substances. Calculate the solubility of each in terms of grams of solute per 100 ml of solution.

SUBSTANCE	SOLUBILITY-PRODUCT CONSTANT
a. $Mg(OH)_2$	1.5×10^{-11}
b. $BaCO_3$	8.3×10^{-9}
c. Ag_2CrO_4	8.8×10^{-12}
d. AgCN	2.2×10^{-12}

CHAPTER 26

THE COLLOIDAL STATE OF MATTER

The Colloidal State · We all know that coarse sand shaken up with water quickly settles when we stop shaking the mixture. The finer the sand, the more slowly it settles. If we powder it fine enough and then stir it into water, it will not settle at all; for the particles will be so small that they will be kept in constant motion by collision with the fast-moving molecules of the water. If we could powder the sand into individual molecules and stir them into water, we should have a true solution.

Atoms and ions are about 10^{-8} cm, or 1 angstrom unit (Å), in diameter; in some cases they are several times as large as this (page 34). The various molecules that we have thus far considered, whether in the gaseous, liquid, or solid state, or in solution, have not been very much larger than the atoms, not more than about 10^{-7} cm (10 Å) in size. In this chapter we shall be interested in those very fine particles that range in size from 10^{-7} cm up to 10^{-5} cm, just too small to be seen in the best microscopes. Particles whose sizes lie in this range are *colloids*, and matter existing in this state of subdivision is said to be in the *colloidal state* (Fig. 26-1).

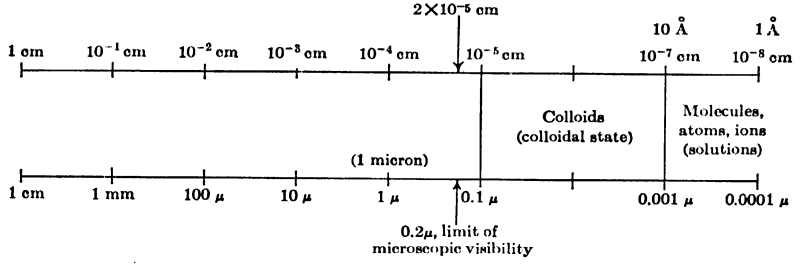


Fig. 26-1. Range of Colloidal-Particle Size, 10^{-7} to 10^{-5} cm · Note that 1 micron (μ) = 0.001 mm, and 1 angstrom unit (Å) = 10^{-8} cm, or 10^{-4} μ

It was formerly thought that a certain group of substances, nearly all of an amorphous character, were the only ones that could assume the colloidal state; and they were called *colloids* (Greek *kolla*, meaning "glue"). Contrasted with the colloid was the *crystalloid*, which formed a true solution and could not be obtained in the colloidal state. We know now that any substance can be obtained in the colloidal state in any liquid in which it is but little soluble. It is merely a question of bringing the substance into the proper state of subdivision. Massive matter may be put into the colloidal state by grinding or powdering, as in

the case of the sand grains above. The smaller particles, atoms and molecules, may flock together, coagulate or crystallize, and so grow into particles large enough to come within the colloidal range. Some giant molecules, like those of the high polymers, the proteins, cellulose, and rubber, which we shall discuss in later chapters, are large enough, as single molecules, to be colloids (Fig. 26-3).

Although colloidal systems composed of solid particles dispersed in a liquid are the most common type, there are other types, such as liquid or solid particles dispersed in a gas and liquid particles dispersed in a liquid. The particles and the medium in which they are suspended constitute a *colloidal system*. The particles are said to be *dispersed* in the medium or in the *dispersing* phase. The term *colloidal solution* cannot properly be used; we use the term *colloidal sol* or *colloidal dispersion* instead.

Ultracentrifuge · Colloidal particles are so small that they do not settle out of a suspension under the pull of gravity (Fig. 26-2 A); but they can be made to settle in a *centrifuge* (26-2 C).

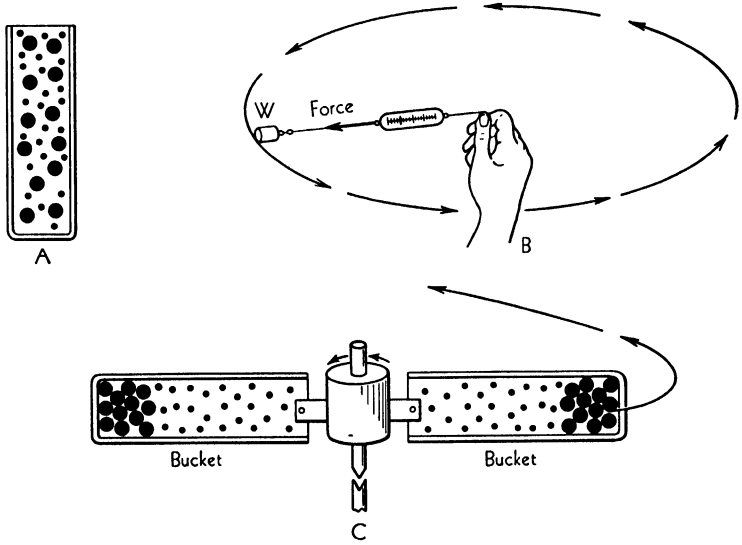


Fig. 26-2. Colloidal Particles · Showing, at *A*, a suspension of large and small colloidal particles; at *B*, a whirling weight, *W*, on the end of a string; and at *C*, spinning centrifuge buckets, with larger colloidal particles settling faster than the smaller ones

If one whirls a weight *W* attached to the end of a piece of string, as in Fig. 26-2 B, one can feel the centrifugal force as the weight tends to pull away; and one can measure the force with a spring balance tied into the string. The force acting on the weight is directly proportional to the mass of the weight, and to the distance between the weight and the center of rotation (that is, the length of the string), and to the square of the number of revolutions per second. This

means that at 10 revolutions per second the force is 100 times as great as at 1 revolution per second.

In a *centrifuge*, like that pictured in Fig. 26-2 C, it is possible to attain a very high velocity of spin, using an air turbine or an electric drive; and the centrifugal force acting on tiny particles suspended in water in the buckets of the centrifuge can become extremely large. For instance, at 60,000 rpm (or 1000 revolutions per second) the force, at 10 cm from the center of rotation, that is pulling a particle through the water to the bottom of a bucket is about 400,000 times as great as would be the pull of gravity on the same particle; and the force is greater for the heavier particles.

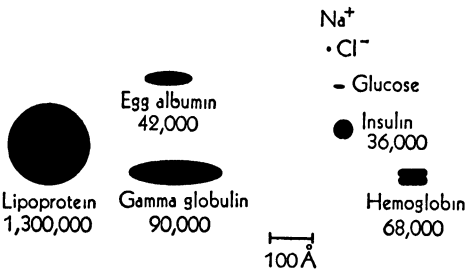
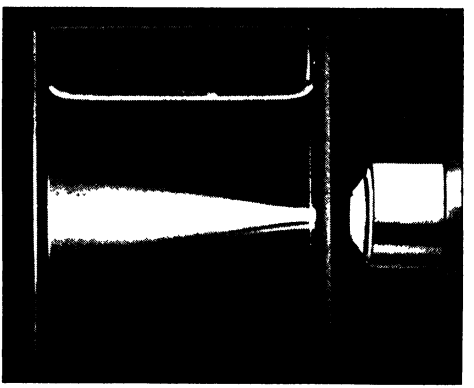


Fig. 26-3. Proteins Showing shape, size, and molecular weight of several large protein molecules in the colloidal range

One can now readily understand how it is possible to cause the tiny particles of a suspension that do not settle at all under the pull of gravity to settle out in a centrifuge; and how, since the larger (heavier) particles settle more rapidly than the smaller (lighter) ones, they can even be separated. Further, from the rate at which they settle their approximate size can be determined. It was by such means that the sizes and molecular weights of the colloidal particles pictured in Fig. 26-3 were obtained.

The Tyndall Beam · The air in a room contains many particles of colloidal size that are too small to be seen as definite individuals, even with a microscope; but if the room is dark and a beam of sunshine enters through a small hole in a curtain, these minute particles can be seen as bright, flashing points, or motes, in the sunbeam.

The English physicist Tyndall showed that in like manner many liquids which under ordinary circumstances appear to be perfectly clear, and even colorless, may in reality contain a great deal of finely suspended matter not removable by ordinary filtration. It is only necessary to pass a strong beam of light through the liquid, in a dark room (Fig. 26-4). In the absence of suspended matter the beam of light has no visible path



Atlas Powder Co

Fig. 26-4 · A Beam of Light Focused by a Lens and Shining through a Colloidal Dispersion, Showing the Tyndall Beam

through the liquid. In the presence of suspended matter, as in the case of the dust particles, light is reflected by these particles. All of them become visible sources of light. This bright path of light through a liquid is called the *Tyndall beam.* Although the Tyndall beam is characteristic of the colloidal state, care must be exercised in using it as a *test* for the presence of colloidal matter. Dust particles in a true solution will cause it to show a Tyndall beam. Pure solutions and solvents may show a very *faint* Tyndall beam in the absence of colloidal matter.

Ultramicroscope · The German chemist Zsigmondy perfected an instrument, called the *ultramicroscope*, that greatly magnifies this Tyndall beam. Its essential parts are a small cell of glass or quartz to hold the colloidal dispersion, a powerful source of light to send a pencil of rays through the cell, and a good microscope so mounted as to look upon the colloidal dispersion at right angles to the beam of light and against a dark background (Fig. 6-16). The minute colloidal particles are seen *not as objects* but as bright specks of light moving in zigzag paths and at greatly differing speeds (Fig. 26-5).

Brownian Movement · As early as 1827 the English botanist Brown, while examining microscopically fine grains of pollen suspended in water, noticed that they kept up a curious zigzag motion, which became known as the *Brownian movement* (p. 79 and Fig. 6-16); but the cause of this motion remained unexplained for eighty years. It was then shown to be a striking confirmation of our conception of the kinetic energy of the molecules of a gas or a liquid. For, if these molecules of the dispersing phase (liquid) have the high speed that we have calculated for them, their collisions with exceedingly fine particles will impart very considerable and erratic motions (Fig. 26-5) to those particles, even though the latter are many times as heavy as the molecules striking them.

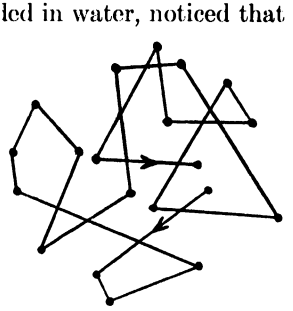
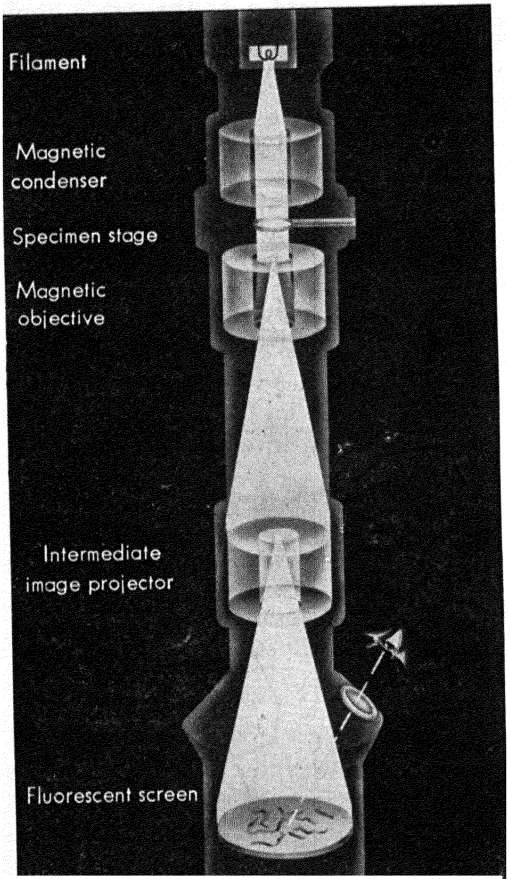


Fig. 26-5. Diagram Showing the Random Brownian Movement of a Colloidal Particle

Limit of Visibility; Electron Microscope · The human eye is not sensitive to light of wave length shorter than about 4000 Å (4×10^{-5} cm) the wave length of violet light. Particles of matter as small as *half* this wave length (Fig. 26-1) cannot be seen clearly in an optical microscope, no matter how powerful the lens system may be. The outlines of the particles appear fuzzy and blurred because of interference between the light waves traveling from the various portions of the particles to the eye.

The electron microscope, recently invented and now in advanced stages of development, operates on much the same principles as the ordi-

nary microscope, but focuses beams of electrons instead of rays of light. The focusing is done with magnetic fields (Fig. 26-6) instead of glass lenses. Electrons act both as particles and as waves, and have a wave length in the electron microscope of the order of 0.05 Å. Because the electron wave length is so small, it is possible to magnify the images of tiny objects, like colloidal particles, much more than in an optical microscope, and obtain sharpness rather than fuzziness in the details of the images. In an electron microscope the magnification may be as great as 200,000 times, as compared with about 2000 times in the best optical microscope. The eye cannot see directly the image, thus magnified, but the magnified image can be made to appear on a photographic film or on a fluorescent screen (Fig. 26-6); and so particles as small as about $\frac{1}{100} \times (2 \times 10^{-5}$ cm), or about 20 Å, the smallest particles of colloidal dimensions, may be observed.

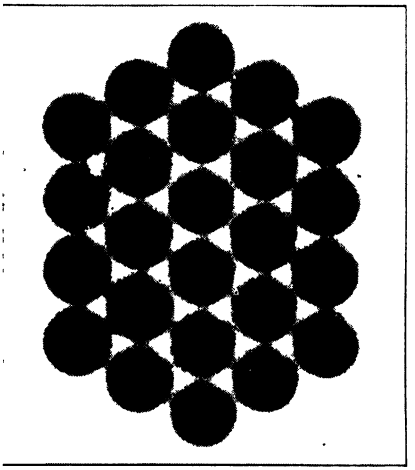


Science Illustrated

Fig. 26-6. Diagram Showing the Beam of Electrons in the Highly Evacuated Chamber of an Electron Microscope The beam is emitted by a hot tungsten filament, passes down through the specimen, is focused in the magnetic fields, and produces a magnified image on the fluorescent screen

The specimen under observation in an electron microscope must be very thin, no thicker than about 1000 Å. Since some materials cannot easily be sliced as thin as this, a "replica" of the surface of a specimen is made by preparing a cast, or impression, of the surface with collodion or with some plastic substance that will reproduce the minutest detail of the surface. The replica is then examined in an electron microscope. The electron-microscope photograph (Fig. 26-7) of the colloidal globules of polystyrene was made directly through a thin section.

The electron microscope reveals to us a submicroscopic world, far smaller than anything that we have hitherto been able to observe. Already we have obtained important information about tiny particles, and we may expect a rapid extension of our knowledge of the minute details of structure of plant and animal tissues, of the bacteria, molds, spores, and other small organisms, as well as an extension of our knowledge of the structure of the surfaces of metals, alloys, and catalysts, and of other surfaces. We may expect also to learn much more about various processes that occur in miniature (as in living cells) - the details of which we do not now understand, but which we should like very much to understand.



Dow Chemical Company

Fig. 26-7. A Photograph of Polystyrene Emulsion, Taken in an Electron Microscope Magnification, 31,500 times. The long-chain polystyrene molecules (p. 580) are coiled up to form tiny globules

Methods of Preparing Colloidal Dispersions · There are many ways of preparing colloidal dispersions, but all these may be classified into two groups:

1. **Dispersion methods.** We may start with an insoluble material in pieces larger than colloidal size and, by grinding or in some other way, reduce it to colloidal particles. We may then mix these particles in the desired medium. Specially designed machines, called colloid mills, are sometimes used to make colloidal dispersions in this way. Almost any sample of ocean water shows traces of gold reduced to colloidal size by the processes of nature.

In many cases we may treat finely divided solids (preferably precipitates) with some reagent that causes them to break up into a colloidal dispersion. Thus, dilute alkali causes the finer particles of clay to form a colloidal dispersion. This action is called *peptization*, and the reagent is said to *peptize* the precipitate.

2. **Condensation methods.** We may start with a substance in true solution or in the gaseous state and bring about the production of a solid or liquid in finely divided form. For example, we may add water to a solution of an oil in alcohol and throw out a cloud of colloidal oil globules; or we may pass hydrogen sulfide into a neutral solution of a salt of antimony (such as tartar emetic) and so produce colloidal antimony sulfide (Sb_2S_3); or we may add an acid to a solution of sodium thiosulfate and

produce colloidal sulfur; or we may treat a very dilute solution of gold chloride with a reducing agent, such as ferrous sulfate or hydrazine chloride, and obtain colloidal gold.

It will be seen that all these processes result in gathering the atoms or molecules of an insoluble substance into clumps or droplets of colloidal size, *which then stop growing.* If growth were to continue, the clumps would become too large to be called colloidal and would form a precipitate, and the droplets would run together into large drops. Some chemists think that the formation of a colloidal dispersion is always the first step in precipitation.

Purification of colloidal dispersions; dialysis. If we filter a colloidal dispersion through even the best of filter paper, no solid is retained on the paper; but if we use a filter made of parchment paper, animal membrane, or cellophane (not the moistureproof variety), we find that the colloidal particles are now prevented from passing through the filter because, among other reasons, the pores of the membrane are smaller than the colloidal particles, but still large enough to permit water molecules and ions of the electrolytes to pass through. By taking advantage of this fact we may purify a colloidal dispersion by a process called *dialysis.* The colloidal dispersion is poured into a filtering bag, *A* (Fig. 26-8), and the bag suspended from a rod, *B*, in a vessel of pure water, *C*. Any impurities that are in true solution diffuse through the membrane, while the colloidal particles remain in the bag, and the dispersion is thus purified. Fresh water may be kept flowing.

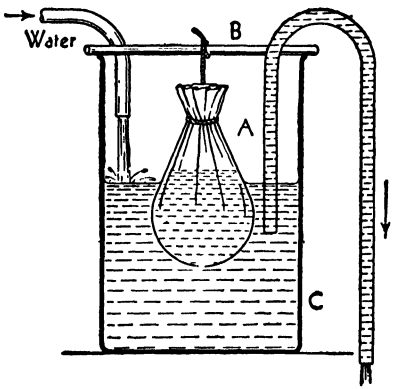


Fig. 26-8. Diagram Showing the Process of Dialysis

Types of Colloidal Systems; Lyophobic and Lyophilic Colloids · Colloidal systems may be divided roughly into two major groups on the basis of the attraction of the colloidal particles for the molecules of the liquid which is the dispersing medium. Colloidal particles for which this attraction is small, such as colloidal gold and the sulfides, are known as lyophobic (liquid-hating) colloids. Suspensions of such colloids do not differ greatly in viscosity from the suspending liquids, often show color, and are readily coagulated by electrolytes. Other colloids have a marked attraction for the liquids in which they are dispersed and are called lyophilic (liquid-loving) colloids. If the dispersing medium is water, these two types of colloids are called hydrophobic and hydrophilic colloids. Hydrophilic colloids include those substances, like gelatin and albumin,

which naturally form colloidal suspensions when mixed with water. Such suspensions are generally much more viscous than pure water and are not easily coagulated by electrolytes.

Classification According to Physical State · Another method of classifying colloidal systems is to group them by the physical states of the dispersed and dispersing phases. There are eight possible combinations:

TYPES OF COLLOIDAL SYSTEMS		
DISPERSED PHASE	DISPERSING PHASE	EXAMPLE
Liquid	Gas	Fog
Solid	Gas	Smoke, dust
Gas	Liquid	Foam
Liquid	Liquid	Emulsions, like milk, mayonnaise
Solid	Liquid	Suspensions, like coffee, muddy water
Gas	Solid	Solid foam, like marshmallow, cake, bread
Liquid	Solid	Butter, oil-bearing shale
Solid	Solid	Many alloys, gold in glass, selenium in glass

Color of Colloidal Dispersions · Many colloidal systems are highly colored, but the color gives us little clue as to what is present. Minute particles of a given size absorb light waves of certain lengths and scatter others. Thus, colloidal gold may be red, blue, green, or violet, according to the size and uniformity of the particles. A little ferric chloride added to boiling water quickly hydrolyzes to a deep-red colloidal hydrated iron oxide.

It takes very little of the colloidal substance to make an intense color. A few milligrams of gold will color a liter of water. A very little of the element selenium added to glass gives it the intense red color of the automobile tail-light. Many colored glasses and glazes owe their color to colloidal material of various sorts, and many gems are colored in the same way. Periods of intensely colored sunsets follow volcanic eruptions that throw vast quantities of colloidal dust into the air.

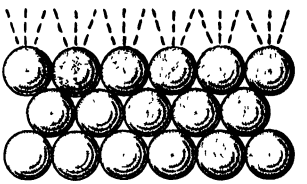


Fig. 26-9. The Particles of a Solid Are Held Together by Attractive Forces Operating within the Body of the Solid · At the surface there are free, unbalanced forces of attraction which will hold an adsorbed layer

Adsorption · By *adsorption* the chemist means the adherence of atoms, molecules, or ions of any kind to the *surface* of a solid (or liquid). The particles of which a solid is composed are held together by attractive forces operating from particle to particle within the body of the solid, and we think of such forces as being saturated and satisfied. But at the surface there are free, unbalanced forces of attraction (Fig. 26-9) which will hold an ad-

sorbed layer. Frequently the adsorbed layer is not more than one molecule deep, and the *tightness* with which it is held depends on the *strength of the forces*; and this depends on the nature of the solid and on the nature of the adsorbed substance. These forces may be relatively weak, like van der Waals forces, or may resemble the stronger forces of chemical bonds. The *quantity* of substance adsorbed depends largely on the *surface area* of the adsorbing material; and since the surface area of a small weight of matter in the colloidal state is relatively large, we may expect to find a relatively large amount of adsorption by colloids.

To see how rapidly the surface area increases as a body is broken into smaller pieces, let us follow the subdivision operation shown in Fig. 26-10. The table lists the values of the surface area as the subdivision is continued down to colloidal size.

Charcoal is a very good adsorbent if it is prepared in such a way that it is porous and has a large pore-surface area. It has been estimated that 1 g of high-grade adsorbent charcoal may have a surface area of from 100 to 1000 m^2 (about one fifth the size of a football field). Such charcoal adsorbs almost incredible quantities of gases or vapors; it may be used

NUMBER OF CUBES	LENGTH OF EDGE	TOTAL SURFACE AREA
1	1 cm	6 cm^2
10^3	1.0 mm	60 cm^2
10^6	0.1 mm	600 cm^2
10^9	0.01 mm	6000 cm^2
10^{12}	1.0 μ	6 m^2* (64.6 sq ft)
10^{15}	0.1 μ	60 m^2
10^{18}	0.01 μ	600 m^2
10^{21}	0.001 μ	6000 m^2 (1.5 acres)

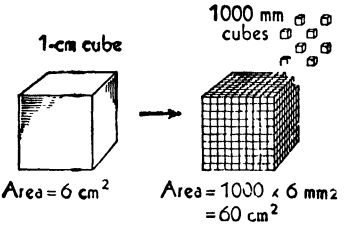


Fig. 26-10. A Diagram Showing Increase of Surface Area as Subdivision Increases

*m^2 = square meters.

in gas masks to adsorb poisonous gases of certain kinds from the air. Platinum and some other metals adsorb hydrogen gas. Dried silica adsorbs water vapor and other gases. Nearly all amorphous solids adsorb most gases and vapors to some extent. Adsorption is sometimes *selective* in character. A given solid will adsorb some substances but not others.

Many catalysts depend for their efficiency on their adsorbing ability, bringing the reacting substances together at high concentration within their pores, or adsorbing one component in a reversible reaction.

Some solids, suspended in solutions, will adsorb dissolved materials

from the liquids. The metallic oxides adsorb dyes to form *lakes* or to act as *mordants*. Fuller's earth adsorbs the coloring matter from corn (maize) oil in the refining of the latter for use as a salad oil; bone char and specially prepared charcoals will adsorb the coloring matters from raw sugar solutions, and so clarify them.

Electric Charge of Colloidal Particles · Colloidal dispersions, even when freed of ordinary electrolytes by dialysis, can be observed under an ultramicroscope to move toward an electrode when a potential is applied; or, if a colloidal dispersion is colored, the movement can be observed without a microscope. This is direct evidence that the colloid particles carry electric charges. Some colloidal particles, including most of the metallic oxides, are positively charged and migrate to the cathode; others, including many metallic sulfides, gold, platinum, silver, and silicic acid, are negatively charged and migrate to the anode. It appears probable that one manner in which colloidal particles get their charges is by the adsorption of some simple ion already existing in the solution, much as a cork might have a tack pressed upon it. In an electric field the imprisoned ions are attracted to the electrode, dragging the whole colloidal clump along, just as the tacks would be attracted by a magnet and carry the cork along with them.

Coagulation of Colloids · Colloidal particles of a given material carrying electric charges of the same sign tend to repel each other. This is one reason why they do not settle. This repulsion prevents the little particles from uniting to form larger ones which would ultimately produce a precipitate.

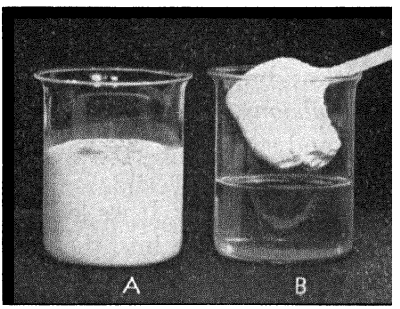


Fig. 26-11. Coagulation of the Rubber in Rubber Latex Beaker *A* contains latex of the rubber tree. A little acetic acid has been added to the latex in *B*. The rubber particles coagulate and cling to a stirring-rod, as shown

If we add an electrolyte to a colloidal dispersion, the large number of charged ions now present tends to diminish this repulsion. The charged colloidal particles attract ions of opposite sign, and the charges on the particles are thereby neutralized. Many such particles then unite to form a precipitate, and the process is called *coagulation*. The silt that deposits at the mouth of a river is due to the precipitation of the colloidal material in river water by the large concentration of salts in the water of the ocean. The little rubber globules, negatively charged, in the milk-like rubber latex are coagulated by the hydrogen ions of acetic acid (Fig. 26-11).

In producing coagulation, bivalent ions are more effective than univalent ones, and trivalent ions are still more effective. This is one of the reasons why aluminum sulfate is used in the clarification of city water supplies. If we mix two colloidal systems containing particles of opposite sign, such as colloidal iron oxide (positively charged) and antimony sulfide (negatively charged), they mutually precipitate each other in electrically equivalent quantities. Two colloidal sols (p. 467) of the same sign have no precipitating effect upon each other.

Protective Colloids · Sometimes a colloidal sol that is naturally unstable is made much more stable by the addition of some other colloidal substance. The latter colloid, which is usually hydrophilic, and readily dispersed in water (p. 472), is called a *protective colloid.* For example, the coloring matter of black ink is frequently a rather unstable colloidal sol, and gum arabic or some similar material is sometimes added as a protecting colloid to keep the coloring matter from precipitating. In making photographic plates gelatin is added to the colloidal silver salts to keep these dispersed as sols. Gelatin and gold will stick to each other. If they are dispersed in water, and if the gelatin colloidal particles are relatively small, they will coat the gold particles; but if large, they will be coated by the gold (Fig. 26-12).

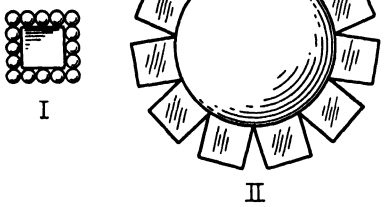


Fig. 26-12. (I) A Gold Particle Coated with Gelatin and (II) a Larger Gelatin Particle Coated with Gold

Emulsions · If we pour together two liquids that do not dissolve in each other and shake the two violently, we get a milky-looking fluid called an *emulsion.* This consists of very minute drops of the one liquid dispersed through the other. If we let the emulsion of an oil in water stand, it will very soon separate into the original liquids (Fig. 26-13 A). To make an emulsion permanent we must add a third substance of a certain kind, slightly soluble in each liquid. This is called the *emulsifying agent.* It seems to form a little skin over the surface of the drops and prevents them from running together into big ones (Fig. 26-14). Milk is an emulsion of butterfat in water, with casein as the emulsifying agent. When the milk turns sour, because of the formation of lactic acid, and the casein is coagulated, the butterfat is easily collected into large lumps of butter. Most of our common disinfectants and sheep dips owe their properties to cresol emulsified in water, with a small percentage of soap as the emulsifying agent. In mayonnaise, olive oil is emulsified in water (usually with a little vinegar added) by the colloidal yolk of egg, forming a

stiff, almost jellylike, product. Cod-liver-oil emulsions contain casein as the emulsifying agent. The fluids that form the webs of spiders and the cocoons of silkworms are secreted as emulsions that almost at once dry to form very fine filaments.

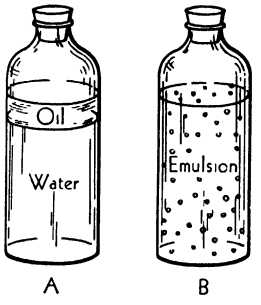


Fig. 26-13. A, Separated Oil and Water Layers; B, Emulsion · When oil and water are shaken together, the oil soon separates in a layer at the top (*A*); if a little soap is added to the oil and water and the mixture shaken, the emulsion becomes more permanent (*B*)

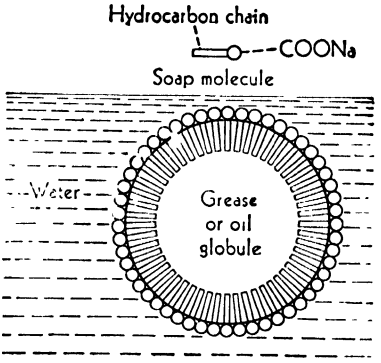


Fig. 26-14. Emulsifying Film of Soap like Sodium Palmitate · Globules of grease or oil are emulsified by being coated completely with a film of soap molecules. The hydrocarbon chains of the soap molecules (p 539) dissolve in the oily globules, and the —COONa groups place themselves outside, in contact with the water

Butter is an emulsion of water droplets in semisolid butterfat, and many lubricating greases are of this same character. The question as to which liquid forms the dispersed droplets and which is the medium for the dispersion is largely determined by the nature of the emulsifying agent employed. The agent seems to act by changing the surface tension of the two liquids to different extents, and surface tension is an important factor in emulsions. In general, a water-peptizable colloid like sodium stearate will give an emulsion of oil in water, whereas an oil-peptizable colloid like calcium stearate will give an emulsion of water in oil.

Jellies · Sometimes minute colloidal particles seem to unite into threads or beads, to form a network of filamentlike structure that takes up and holds a large amount of water in much the same way that a sponge holds water. When this happens, the whole dispersion is likely to set to a more or less rigid form called a *jelly* or gel. If we add hydrochloric acid to a solution of sodium silicate, the dilute dispersion of silicic acid sol which is first formed soon sets to a firm jelly. In fruit jellies it is a constituent of the unripe fruit, called *pectin*, that serves to form the supporting structure. In gelatin or glue the jelly may be dried out to a very compact form; but when it is dispersed in hot water and cooled, a

jelly is once more obtained. When the silicic acid gel is dried, it forms solid, infusible lumps resembling a gum, and this cannot be dispersed by ordinary heating in water. These lumps are extremely porous, owing to the original structure of the jelly, and are very active as catalysts in many gaseous reactions. Soap is a partially dried jelly, and many minerals such as agate, flint, and opal are dry silica gels. Photographic emulsions and many high explosives are jellies. Almost any sparingly soluble substance that does not crystallize too readily may be obtained in the form of a jelly. The so-called *solidified alcohol* consists of a porous soap and alcohol, the soap acting as a sort of sponge to hold the alcohol.

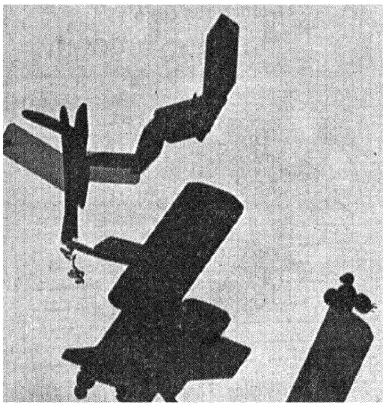


Fig 26-15. An Electron-Microscope Picture of Molybdenum Oxide Smoke Particles Magnification, 16,400 times

Smokes · Smoke is a dispersion of solid particles of colloidal size (Fig. 26-15) in a gas, particularly air. The formation of smokes gives rise to many problems in chemical industry. When a substance such as phosphorus burns in air to form a product which is volatile at the temperature reached in combustion, but which condenses to a solid without liquefying, or when vapors are suddenly chilled below their melting points by cold air (as in distilling zinc or sulfur), the product usually forms a finely divided smoke. So, too, when dry gases combine chemically to form a solid, a smoke is usually formed; an example is the white smoke of ammonium salts that often characterizes the atmosphere of chemical laboratories.

It is often very difficult to condense the particles of a smoke into coherent form, and this fact is of enormous industrial importance. Many precious materials literally "go up in smoke" from the stacks of smelters; much zinc is lost as a smoke of zinc oxide in brass foundries; valuable potassium compounds are lost in the smoke of cement burners; and ordinary carbon smoke causes enormous losses to individuals but corresponding profit to laundries.

The Cottrell Process · All the fine particles in smoke are electrically charged, or become so when placed in a suitable electric field. Taking advantage of this fact, Cottrell devised a method for settling smokes that has come into wide use. The air, laden with smoke, is passed between two electrodes, one a plate and the other a series of points (Fig. 26-16), maintained at a high difference of electric

potential. The charged particles are attracted to the plate, are discharged, and then collect into coherent dust that quickly settles. Great use is made of this process in recovering valuable materials from the stacks of smelters and from cement kilns, as well as in abating smoke nuisances (Fig. 26-17) and in preparing dust-free air for elaborate air-conditioning installations.

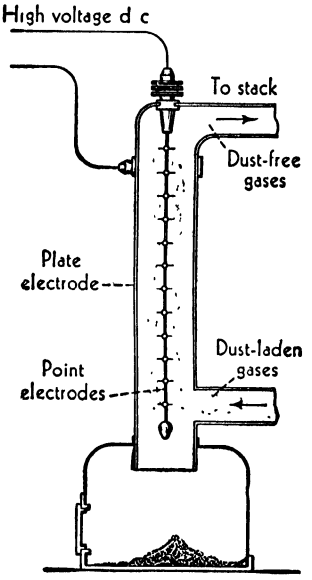


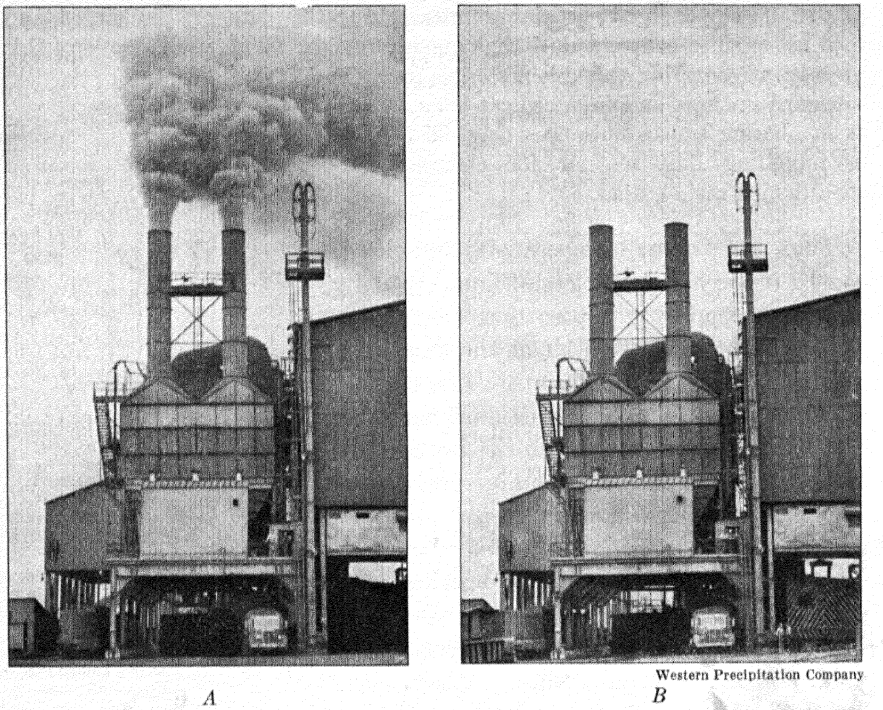
Fig. 26-16. Diagram of a Cottrell Precipitator

Fogs and Foams · Fogs, mists, and clouds consist of very fine droplets of liquid (usually water) suspended in air, so that they correspond to *emulsions* with air as the dispersing medium. They are usually formed by contact of supersaturated vapors with dust particles; the solid particles serve as nuclei for condensation of the vapor. Foams are gas bubbles dispersed through a liquid—for example, whipped cream, meringue, the foam of soapy water, and the froth on beer. Sometimes these minute gas bubbles are dispersed through what we should usually consider a solid, and make it pure white. Many white flowers, like lilies, are said to owe their whiteness to dispersed gas bubbles, as does also white hair. Other examples of solids containing dispersed air bubbles are milky quartz, pumice, and lava.

The Field of Colloids · It will be seen that an understanding of the fundamental principles of the colloidal state is of the greatest importance. In some cases we wish to break up this condition and bring substances into true solution or to crystallization. In a very much larger number of cases the desirable properties of substances lie in the fact that they *are* colloidal, and we wish to produce or maintain this state.

Many plastic materials are in part colloidal or closely approach this condition. These include pastes, glues, gums, shellacs, varnishes, some cements, rubber, Bakelite, celluloid, clays, etc. The process of "setting" seems in many instances to involve jelly formation.

In the organic world the fundamental living cell consists of a colloidal wall enclosing a liquid dispersion resembling a jelly. All organs and structures composed of cells have therefore a colloidal character. Consequently physiology and medicine deal constantly with colloidal problems, for nearly all biological processes, such as nutrition, digestion, and secretion, depend in some way upon the properties of colloids. All indus-



Western Precipitation Company

A B

Fig. 26-17. The Cottrell Process *A* shows dust and fumes arising from three large electric furnaces; *B* shows the same plant operating with the Cottrell precipitator

tries that make use of organic materials, such as those engaged in the manufacture of paper, photographic plates and films, textiles, and leather, are colloidal industries.

Nearly all the food we eat, as well as the soil on which it is grown, is colloidal, so that the preparation of food of all sorts is a colloid art. All preparation of finely divided materials, such as printer's ink and paints, involves colloid problems. It is hard to overemphasize the importance of extending our knowledge in this field.

QUESTIONS

1. Define (*a*) *colloidal particles*, (*b*) *dispersed phase;* (*c*) *dispersing medium*, (*d*) *adsorption;* (*e*) *Tyndall beam;* (*f*) *Brownian movement*, (*g*) *peptization*, (*h*) *dialysis;* (*i*) *lyophobic colloid;* (*j*) *lyophilic colloid;* (*k*) *jelly;* (*l*) *protective colloid;* (*m*) *emulsion;* (*n*) *emulsifying agent;* (*o*) *gel.*

2. (*a*) Compare the size of colloidal particles with that of atoms and ions. (*b*) Is it possible to have molecules whose size is within the range of that of colloidal particles? (*c*) If so, give some examples of such molecules.

3. (*a*) Explain the principle of the ultramicroscope; of the electron microscope. (*b*) What is the size of the smallest object that can be detected clearly with the ordinary microscope; with the electron microscope? (*c*) Why does the Tyndall beam reveal the presence of particles that cannot be seen with an ordinary microscope? (*d*) Does an ultramicroscope reveal the outlines of the actual particles?

4. (*a*) Why should the path of a colloidal particle be a zigzag of straight lines rather than a curved line? (*b*) Why do the points of light in the field of an ultramicroscope move so much faster than the particles to be seen with an ordinary microscope?

5. How does a dialyzing membrane differ from an osmotic membrane?

6. How can you prove that the particles of a colloidal dispersion are electrically charged?

7. (*a*) How could you prove that a hot dilute solution of ferric chloride contains colloidally dispersed iron oxide? (*b*) What reagent would you use to coagulate the dispersion?

8. Many compounds used as fertilizers are very soluble in water. (*a*) Why are they not quickly washed out of the soil by rains? (*b*) What evidence have you that they wash out slowly?

9. Some liquid medicinal materials, such as cod-liver oil, are often prescribed in the form of emulsions. Can you see any advantage in this?

10. On the basis of the principles studied in this chapter explain why (*a*) a curd is formed when milk is poured on sour fruit; (*b*) soap serves as a cleansing agent; (*c*) electrically charged plates in a chimney will eliminate the smoke or dust; (*d*) fruit juice will form a jelly; (*e*) water may remain muddy for a long period of time; (*f*) mayonnaise dressing does not separate into oil and water; (*g*) river deltas are formed where the rivers empty into the oceans.

PROBLEM

A cube of gold 1 cm on an edge is broken up into small cubes 1×10^{-7} cm on an edge. (*a*) Calculate the total surface area of the gold in each case. (*b*) Compare the total area of the small gold cubes (1×10^{-7} cm on an edge) with some familiar area, such as that of a city block or a football field. (*c*) What is unusual about the ratio of surface area to volume of colloidal particles?

CHAPTER 27

CARBON AND SILICON

The carbon family consists of five elements: carbon, silicon, germanium, tin, and lead, and falls rather sharply into two groups. The first two elements are nonmetals; the last three are metals. Germanium, tin, and lead will be considered later (Chap. 44); but there is considerable advantage in studying carbon and silicon together, in this chapter. While carbon and silicon are nonmetals, they combine readily with either metals or nonmetals. Their chemistry is best understood by assigning to each a covalence of four without regard to oxidation state (though carbon is found in a few compounds, such as carbon monoxide, with a covalence of two).

Role in Nature · The elements carbon and silicon play a large role in nature. The "organic" world, the world of living and growing things, is largely founded on compounds which have carbon as their central element. The "inorganic" world, the world of the rocks and the inanimate substances of the earth's crust, is in large part based on compounds of silicon, particularly the compounds of silicon with oxygen. The importance of the compounds of carbon and silicon lies in the fact that these compounds also often have very large molecules which are chainlike or threadlike, or exist in a network pattern. It is these structural features which account for the particular qualities of some of the rocks, the toughness of wood, the strength of silk, and the elasticity of rubber.

In studying the chemistry of these compounds, therefore, we are attempting to gain an insight into the structural features of the world about us.

Occurrence of Carbon and Silicon · In the free condition carbon is found in nature in several forms. Diamond is practically pure carbon, as is graphite. The various kinds of coal are complex mixtures of free carbon, together with a great variety of material derived from plant life and with mineral impurities. The natural compounds of carbon are exceedingly numerous, and occur in the form of gases, liquids, and solids. Carbon dioxide (often called carbonic-acid gas) is its most familiar gaseous compound. Natural gas and petroleum are composed principally of hydrocarbons, which are compounds of carbon and hydrogen. The carbonates, especially calcium carbonate in the form of marble and limestone, constitute great strata of rocks and are found in almost every lo-

cality. Living organisms, both plant and animal, contain a large percentage of combined carbon; and the number of compounds which go to make up all the vast variety of animate nature is almost limitless.

Silicon does not occur in nature in the free state. Its compounds are not found in air, nor to any considerable extent in water; but the solid crust of the earth is estimated to contain about 27 per cent of silicon in the form of compounds (p. 31). All varieties of granite, sandstone, shale, clay, and marl contain large percentages of the element. Limestone and dolomite are the only important geological formations measurably free from it. In the realm of inorganic nature it is the central element, just as carbon is of fundamental importance in organic nature.

The Free Elements

Preparation · Since carbon occurs in the free state in coal, graphite, charcoal, and in other forms, it is not usually necessary to undertake its preparation, except when a very pure carbon is needed.

Silicon is best prepared in the laboratory by heating the dioxide with aluminum powder:

$$3\ SiO_2 + 4\ Al \longrightarrow 3\ Si + 2\ Al_2O_3$$

The silicon dissolves in the excess of melted aluminum. When the solution has cooled, the aluminum is dissolved in hydrochloric acid, and the silicon is left in the form of shining metallic needles. Reduction of the silicon dioxide with carbon under suitable conditions gives silicon of about 98-per-cent purity. By reducing a mixture of the oxides of silicon and iron with carbon, an alloy of the two elements is obtained, called ferrosilicon. This alloy, as well as the purer silicon, has important uses in the metallurgy of iron.

Properties of free carbon and silicon · The two forms of pure carbon—diamond and graphite are highly crystalline, and are actually pure carbon or nearly so. The free carbon in other substances, such as coal, coke, charcoal, carbon black, and bone black, is often described as amorphous.

Diamond · This form of carbon has long been known and highly prized as a gem. Diamonds are found in several localities, especially in South Africa, the East Indies, and Brazil. The crystals belong to the isometric system, and the natural crystals are usually rough and superficially stained; to bring out the brilliancy of the gem the natural crystal is cut in such a way as to refract the light most effectively. The density of the diamond is 3.51. It is the hardest substance known, and is used

as an abrasive. Few chemical reagents have any action upon the diamond, but when heated in pure oxygen or in air it blackens and finally burns, forming carbon dioxide.

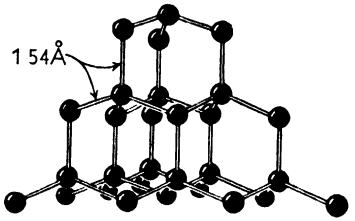


Fig. 27-1. Crystal Lattice of Diamond

In a normal year the yield of diamonds is about 20 million carats. (A carat is 200 mg.) About 80 per cent of all diamonds are used in industry, and about 70 per cent of these are used as powder.

Though it had been earlier reported on several occasions that synthetic diamonds had been produced, it had turned out not to be so. But in the year 1954, in the laboratories of the General Electric Company, authentic diamonds, though of small size– about one sixteenth of an inch—were obtained. The diamonds were made at a temperature of 2800° C and under a pressure of 1.5 million pounds per square inch, conditions computed to exist 240 miles down in the earth.

Bone Black, Carbon Black, Lampblack · When bones, which are composed of about 40 per cent organic matter and 60 per cent mineral matter (chiefly calcium phosphate), are subjected to destructive distillation, *bone black* is formed. It consists of finely divided amorphous carbon dispersed through the mineral matter. *Carbon black* is a fluffy, very finely divided powder, the particles of which are 0.025–0.05 micron in diameter. It is made by burning natural gas and directing the flame against moving metal surfaces. The unburned carbon deposits as a black soot on the metal. Its greatest use is in the manufacture of rubber goods (especially tires), to which it adds strength and resiliency. Large quantities are used in making printer's inks, paints, phonograph records, and polishes for shoes and stoves. By burning oils, coal gas, or acetylene in insufficient air a black powder (*lampblack*) is obtained, similar to carbon black. It has been largely replaced by carbon black.

Finely Divided Carbon and Adsorption · Finely divided and porous carbon is remarkable for its property of adsorbing (p. 473) various gases and liquids. The volume of the gas adsorbed depends upon the nature of the gas, on the physical state and source of the charcoal, and on the temperature and pressure during adsorption. Charcoal made from coconut shells, and *activated* while very hot by a mild oxidation with steam, has a very great adsorptive power for gases. Some idea of this adsorbing power may be gained from the fact that 1 volume of a certain coconut charcoal at a pressure of 760 mm adsorbs the following volumes of ammonia at the temperature indicated: 83 volumes at 70°; 96 volumes at 50°; 149 volumes at 20°; and 176 volumes at 0°.

Bone black and activated charcoal adsorb many organic substances from their solution in water. Many dyes are adsorbed in this way, and in the manufacture of sugar the solutions are decolorized before crystallization by filtration through filters of charcoal or of bone black.

Gas Masks · The use of poison gases in war has made it necessary to devise gas masks for the protection of troops. These are fitted to the face in such a way that all inhaled air has to pass through a light metal box (canister) filled with layers of various materials, the chief of which is activated charcoal. These materials either adsorb or combine with the poison gases, and great efficiency is attained.

Graphite · This form of carbon is found in nature in large quantities, especially in Ceylon and Siberia, and in some localities of the United States, Mexico, and Canada. The crystals belong to the hexagonal system. Graphite is a shining black substance, very soft and greasy to the touch. Its density is about 2.25. It varies somewhat in properties, according to the locality in which it is found and the impurities present. When any form of carbon is heated in an electric furnace to a temperature of 3500°, it rapidly vaporizes, and the vapor always condenses in the form of graphite.

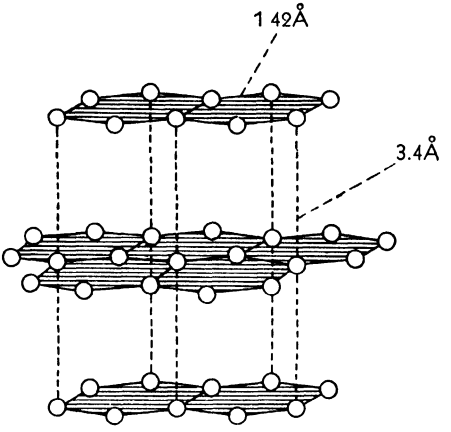


Fig. 27-2. The Arrangement of Carbon Atoms in the Graphite Crystal

Graphite is used in the manufacture of crucibles, as a lubricant, and as a protective cover for iron in the form of a paint or polish, such as stove polish. It has long been used in the manufacture of lead pencils, a fact indicated by its name, which is derived from a Greek word meaning "to write."

Properties of Carbon · The varieties of carbon differ in many respects, such as hardness, density, and color, as a result of their crystalline condition, their fineness of division, or the presence of impurities. They are all odorless, tasteless solids, insoluble in all ordinary solvents. Carbon is slightly soluble in some melted metals, and of these, iron is the best solvent. Carbon cannot be melted, but at an intense heat it passes directly from a solid into a vapor.

Properties of Silicon · The element is obtained in crystals of the isometric system, in form resembling diamond. They are very hard, easily

scratching glass, and have a density of 2.4. They melt at 1420°. A lump of the element is very brittle and breaks with a crystalline fracture, which has a metallic, silvery appearance.

Chemical Properties of Carbon and Silicon · At ordinary temperatures carbon is a very inactive substance, but at higher temperatures it combines directly with most of the elements, such as oxygen, hydrogen, sulfur, silicon, chlorine, and many metals. Hot carbon is a powerful reducing agent.

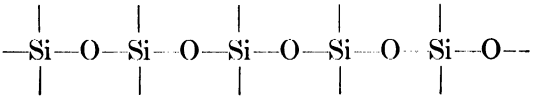
Silicon likewise is relatively inactive at ordinary temperatures. However, it is readily attacked by the halogens, forming gaseous halides. Solutions of strong bases, such as sodium hydroxide, readily dissolve it, evolving hydrogen and forming soluble silicates—a reaction that has been used in the commercial preparation of hydrogen:

$$4\ NaOH + Si \longrightarrow Na_4SiO_4 + 2\ H_2$$

Silicon is not attacked by oxygen as easily as would be expected, considering the difficulty with which its oxide is reduced. This inactivity is due to the high melting point of silicon and to the fact that a thin film of nonvolatile oxide forms upon the surface, which protects it from further action. At high temperatures silicon combines with the great majority of elements and forms silicides, such as that of magnesium (Mg_2Si). Of particular interest is its compound with carbon, silicon carbide (SiC), a substance nearly as hard as diamond, prepared by heating sand and coke, and known under the trade name Carborundum.

The Compounds of Carbon and Silicon

Carbon and silicon occur in Group IV B of the periodic table, a position intermediate between the metals and the nonmetals. Their atoms have four valence electrons, and the bonds formed between their atoms and those of other elements are almost exclusively covalent bonds. Carbon atoms form covalent bonds with other carbon atoms, resulting in compounds containing chains and rings of carbon atoms. This characteristic of carbon will be discussed in detail in later chapters. Silicon-to-silicon bonds are not nearly as common in nature as carbon-carbon bonds. Silicon, on the other hand, shows a strong tendency to form chains with oxygen, in which are found alternating silicon and oxygen atoms:



Such a structure is to be found in many rocks and in glass, china, cement, and other ceramic materials. The most important difference between carbon and silicon in their compounds lies in the inability of silicon to form double bonds. This difference is well illustrated by a study of the oxides, CO_2 and SiO_2.

Carbon Dioxide and Silicon Dioxide · The normal covalence of carbon and silicon is 4. One expects the formulas for the oxides to be CO_2 and SiO_2 respectively. Because carbon and silicon are adjacent members of the same family in the periodic table, one would further expect these oxides to resemble each other in physical and chemical properties. Yet, in many respects they are very unlike, particularly in their physical properties. Carbon dioxide is a colorless gas with a molecular weight of 44, corresponding to the simple formula, CO_2. Silicon dioxide is a hard solid, with an extremely high melting point and a molecular weight so high as to be indeterminable. Its molecular weight does not correspond to SiO_2, but to $(SiO_2)_x$, where x is a very large number; in fact, any lump of $(SiO_2)_x$ may almost be thought of as being one huge molecule. The reason for the difference is that in carbon dioxide the atoms are bound by double bonds: O=C=O. In silicon dioxide, however, silicon-oxygen chains, such as that pictured on page 486, are bound through silicon-oxygen bonds to other silicon-oxygen chains, making giant molecules (pp. 350, 497).



Fig. 27-3. Molecule of Carbon Dioxide

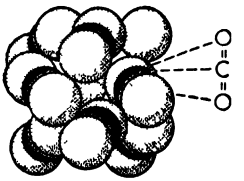


Fig. 27-4. Crystal Lattice of Carbon Dioxide

The Hydrides of Carbon and Silicon · As might be expected, carbon and silicon form the simple hydrogen compounds, CH_4 and SiH_4 respectively, called methane and silicomethane, or silane. Methane is a gaseous compound, the chief constituent of natural gas. Silane is similar to methane in its physical properties. Both elements, however, form other compounds with hydrogen, such as C_2H_6, C_6H_{14}, $C_{20}H_{40}$, Si_2H_6, Si_3H_8, etc. The hydrides of silicon do not occur in nature, and can be prepared only with difficulty. The hydrides of carbon, however, called *hydrocarbons*, are found in nature in petroleum, turpentine, and rubber, are formed in many natural processes, and are found in such industrial materials as coal tar. Their abundance, the complexity of their formulas and the fact that all the products of growth in the organic world can be related to them structurally suggest that a special study of the hydrocarbons be made. We will, therefore, devote certain later chapters to this study.

The Chlorides · As with the hydrides, carbon and silicon form chlorides, CCl_4 and $SiCl_4$, as well as some compounds which are considerably more complex. The halogen derivatives of carbon will be considered in more detail later (p. 515); here we shall describe some of the halogen derivatives of silicon.

Silicon Tetrachloride ***($SiCl_4$)*** · This is a colorless liquid which boils at 57.6° and hydrolyzes in contact with air, forming hydrochloric acid and an oxide or hydroxide of silicon. It can be made by direct union of silicon and chlorine, or by conducting the chlorine through a heated mixture of carbon and silicon oxide:

$$SiO_2 + 2\,C + 2\,Cl_2 \longrightarrow 2\,CO + SiCl_4$$

In time of war it has been used to produce smoke clouds for concealing troops and ships.

Silicon Fluoride ***(SiF_4)*** · Silicon fluoride is a gas at ordinary temperatures and is easily prepared by the action of hydrofluoric acid upon silicon dioxide:

$$SiO_2 + 4\,HF \longrightarrow SiF_4\uparrow + 2\,H_2O$$

In a somewhat similar way hydrofluoric acid acts upon silicates, converting both the silicon and the metals into fluorides (p. 274).

Fluosilicic Acid ***(H_2SiF_6)*** · When silicon fluoride is conducted into water, it is hydrolyzed, according to the following equation.

$$SiF_4 + 4\,H_2O \longrightarrow Si(OH)_4 + 4\,HF$$

A part of the silicon hydroxide then dissolves in the hydrofluoric acid:

$$Si(OH)_4 + 6\,HF \longrightarrow H_2SiF_6 + 4\,H_2O$$

The *fluosilicic acid* (H_2SiF_6) is soluble. It is a moderately strong acid and forms soluble, well-crystallized salts with most of the metals. The potassium salt, K_2SiF_6, is very sparingly soluble, and its formation is often employed as a test for potassium ions.

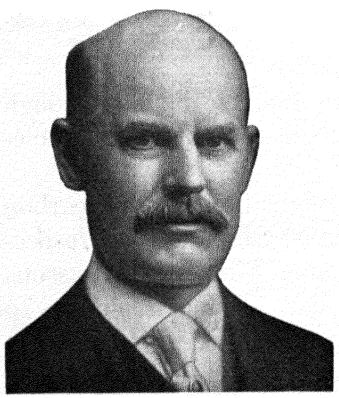


Fig. 27-5. Edward Goodrich Acheson (1856–1931) · An American scientist who developed commercial methods for the manufacture of Carborundum, graphite, and other high-temperature products of great use in the industrial world

Silicon Carbide ***(Carborundum)*** ***(SiC)*** · At the temperature of the electric furnace, silicon combines with carbon to form the *carbide*, SiC, best known under the trade name *Carborundum*. This carbide is made by heating sand and coke in an electric furnace —a process devised by Acheson (Fig. 27-5) in 1891, and extensively carried on at Niagara Falls. The reaction may be expressed in the equation

$$SiO_2 + 3\,C \longrightarrow SiC + 2\,CO\uparrow$$

The carbide so prepared consists of beautiful black crystals, which usually have a brilliant purple iridescence. The color is due to the reflection of light from thin crystalline layers on the surface. The material is almost as hard as diamond and is much used in place of emery for grindstones and polishing powders and also in electrical resistor heaters.

Manufacture of silicon carbide. The furnace in which silicon carbide is prepared is merely a rectangular box built of loose bricks. In the center of each end of this box is an electrode consisting of a carbon rod. The box is filled to the level of the electrodes with the charge, a layer of broken pieces of carbon is spread from one electrode to the other, and the box is then filled to the top with the charge. A cross section of a furnace so charged is represented in Fig. 27-6. *A* is the core of carbon, *B* the mixture of materials. These are coke, sand, a little common salt, and sawdust. The salt assists the reaction in some way, while the sawdust chars and leaves the mass porous, thus aiding the escape of carbon monoxide gas. The broken carbon offers great resistance to the current, and the heat along the carbon core becomes intense. This causes reaction to take place from the center for some distance into the mass. The result is represented in Fig. 27-7. *A* is the core of carbon, surrounded by a core of crystallized carbide, *B*, and this in turn by a layer, *C*, of amorphous carbide and partially reduced products. These are known as *white stuff*, *siloxicon*, or *silundum*, according to their character. They are useful for making furnace linings and firebrick. The material *D* is unchanged.

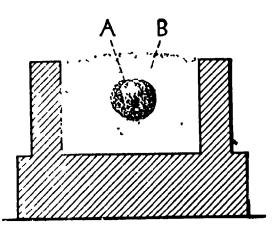


Fig. 27-6. Diagram Showing the Cross Section of a Charged Carborundum Furnace before Heating

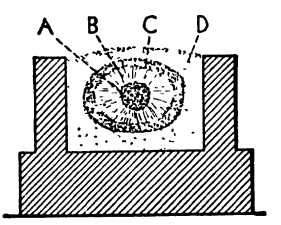


Fig. 27-7. Diagram Showing the Cross Section of a Charged Carborundum Furnace after Heating

The Oxides

Carbon Monoxide · 1. **Preparation.** The extremely poisonous compound carbon monoxide (CO) occurs in the gases issuing from volcanoes. It is formed in different metallurgical processes, and especially when carbonaceous materials, such as coke, charcoal, and gasoline, are burned in a limited supply of air. The pure gas can be prepared in a number of ways, the most important of which is by passing oxygen over hot carbon. When carbon burns under ordinary conditions, the product is carbon dioxide:

$$C + O_2 \longrightarrow CO_2 + 94{,}030 \text{ cal} \qquad (1)$$

If the carbon is very hot and in great excess (in other words, if the supply of oxygen is insufficient for complete combustion), then the carbon dioxide at first formed is reduced to carbon monoxide by the hot carbon:

$$C + CO_2 \longrightarrow 2\,CO - 41{,}250\ \text{cal} \qquad (2)$$

Combining equations (1) and (2), we have

$$2\,C + O_2 \longrightarrow 2\,CO + 52{,}780\ \text{cal} \qquad (3)$$

These reactions take place when hard coal burns in a stove. When the air first comes into contact with the hot coal, carbon dioxide is formed; but as the gas rises through the glowing-hot coal, it is reduced to the monoxide, which burns with a blue flame on the top of the coal, where it comes into contact with more air (Fig. 27-8). If the supply of air is limited, the carbon monoxide passes off as one of the products of combustion.

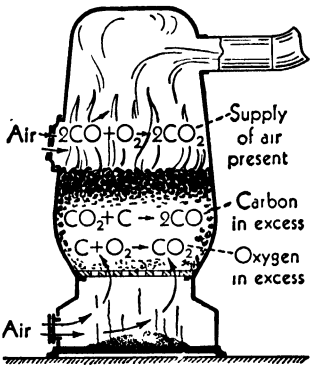


Fig. 27-8. The Formation of Carbon Monoxide from Hard Coal Burning in a Stove

2. **Properties.** Carbon monoxide is a colorless, practically odorless gas. It is 0.967 times as heavy as air. It can be liquefied (boiling point, $-192°$) and solidified (melting point, $-207°$). It is almost insoluble in water, but is absorbed by a solution of cuprous chloride to which has been added either hydrochloric acid or ammonia. It is a fairly active compound, combining directly with a great many substances. It is a strong reducing agent, being oxidized readily by free oxygen and many oxides. For example, when it is passed over heated copper oxide, the copper is reduced to the metallic state. (Compare with the action of hydrogen, p. 94.)

$$CuO + CO \rightleftarrows Cu + CO_2$$

Carbon monoxide also combines with chlorine, forming phosgene, $COCl_2$; and with sulfur to form carbon oxysulfide, COS, and with sulfur, and some of the metals, such as nickel and iron, to form metal carbonyls, such as nickel carbonyl, $Ni(CO)_4$.

3. **The poisonous properties of carbon monoxide.** Carbon monoxide is one of the most treacherous of poisons, since it has neither color nor odor. Its poisonous properties are explained as follows: The oxygen taken into the lungs is loosely absorbed by the red coloring matter of the blood (hemoglobin) and carried to all parts of the body to be available for oxidation. The affinity of this red coloring matter for carbon

monoxide is about 300 times greater than for oxygen, and the compound formed is a stable one; consequently, in an atmosphere containing even a small percentage of carbon monoxide the blood soon loses its ability to absorb oxygen, and death results. A person undergoing slight exercise in an atmosphere containing as little as 1 part of carbon monoxide in 500 parts of air will become unconscious in about an hour; and if such air is inhaled for three more hours, death will result.

Precautions · Since carbon monoxide is generated whenever carbon is burned in a limited supply of air, it is often formed in stoves when the air draft is shut off, especially when hard coal is used as a fuel. It is also formed when gas is burned and the flame is directed against a cold metal surface. It is of the greatest importance that all stoves where gas is burned should be provided with suitable chimney connections and that these connections should be kept in order; otherwise, the carbon monoxide formed may escape into the air of the room and become a serious menace to anyone inhaling it. Many lives are lost each year because of negligence in these precautions.

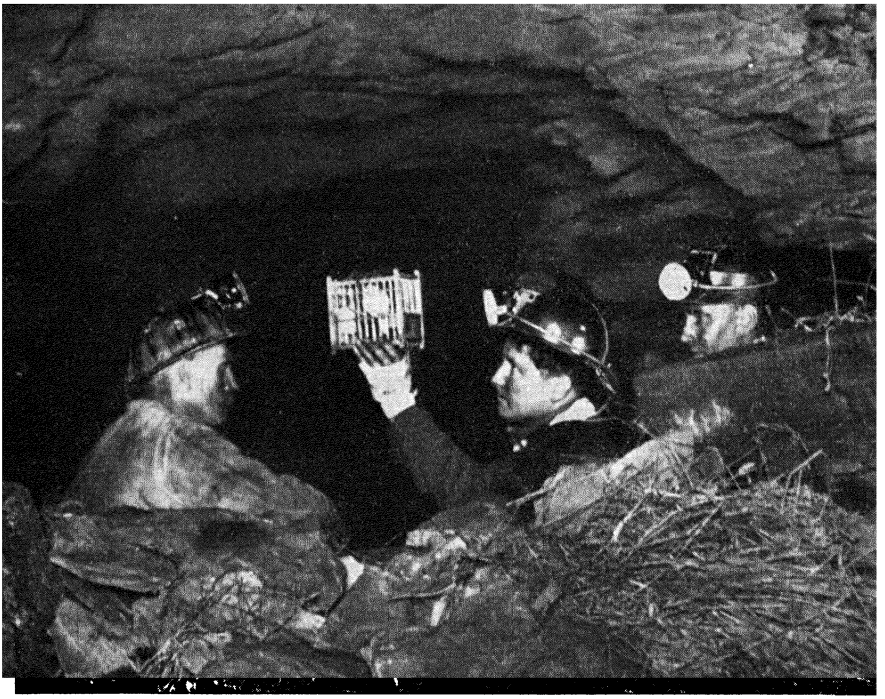
Carbon monoxide is formed in the explosion of gasoline in engine cylinders, forming from 3 to 12 per cent of the exhaust gases. The air in a closed garage becomes dangerous when an automobile engine is allowed to run for even a few minutes.

It is interesting that birds are very sensitive to this gas. In mine explosions carbon monoxide is always formed, and rescuers often carry canaries with them, since the death of the birds warns the rescuers of their own peril (Fig. 27-9).

A number of tunnels have been constructed in congested districts to accommodate automobile traffic. An effective system of ventilation is required in these tunnels to prevent the air from becoming poisoned with the carbon monoxide of automobile-exhaust gases. Extensive experiments were carried out by the United States Bureau of Mines to determine the amount of carbon monoxide that may be present in the air of such vehicular tunnels without endangering the health of those breathing it. These experiments showed the maximum amounts allowable to be 1 part of the monoxide in 2500 parts of air, and this only for persons breathing the air for a period of not longer than one hour.

Carbon Dioxide · The presence of carbon dioxide in the atmosphere and its importance in the growth of plants have been noted previously (page 107). The structure of carbon dioxide has also been discussed (p. 487). We shall here go into its physical and chemical properties in somewhat greater detail.

Properties · Carbon dioxide is a colorless, practically odorless gas, 1.5 times as heavy as air. One liter of it weighs 1.9768 g. Its high density



United States Bureau of Mines

Fig. 27-9. Mine Rescuers Testing for the Presence of Carbon Monoxide with Canaries

compared with that of air may be inferred from the fact that it can be siphoned or poured like water from one vessel downward into another. At 15°, and under ordinary pressure, 1 volume of water dissolves about 1 volume of the gas. Its solubility increases regularly in proportion to the pressure until about 5 atm is reached; beyond this point its solubility increases less rapidly. It is readily obtained in the liquid as well as the solid state.

Preparation of Carbon Dioxide · In the laboratory, carbon dioxide is prepared by the action of an acid, usually hydrochloric, upon calcium carbonate ($CaCO_3$), which is found abundantly in nature in the form of limestone and marble. When hydrochloric acid is added to marble, calcium chloride ($CaCl_2$) and the very unstable compound called carbonic acid (H_2CO_3) are formed. This acid at once decomposes into water and carbon dioxide. The latter, being but sparingly soluble, escapes and may be collected by the displacement of air or water. The equations for the reactions are as follows:

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2CO_3$$
$$H_2CO_3 \longrightarrow H_2O + CO_2$$

The apparatus represented in Fig. 27-10 is convenient and automatic. When the stopcock, *D*, is opened, the acid runs down into *C* and up into *A*, where it comes into contact with the lumps of marble. The carbon dioxide generated escapes through *D*. If now the stopcock is closed, the gas, being unable to escape, collects in *A* and drives the acid away from the marble, down into *C* and up into *B*, so that the action ceases until the stopcock is again opened. This apparatus is known as a Kipp generator.

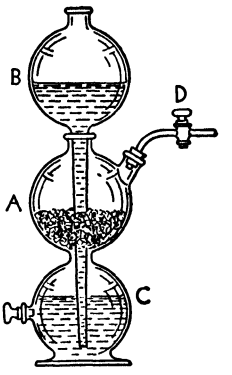


Fig. 27-10. A Kipp Generator

Preparation for Commercial Purposes · For commercial purposes carbon dioxide is obtained from a number of sources. 1. The chief source is the combustion of coal. The products of combustion are sprayed with a solution of sodium carbonate, which reacts rapidly with the carbon dioxide in the gases to form the compound sodium bicarbonate. The latter compound, when heated, evolves pure carbon dioxide and reverts to sodium carbonate, which can then be used over again.

$$\underset{\text{carbon dioxide}}{CO_2} + \underset{\text{water}}{H_2O} + \underset{\text{sodium carbonate}}{Na_2CO_3} \longrightarrow 2\ \underset{\text{sodium bicarbonate}}{NaHCO_3}$$

$$2\ NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + H_2O + CO_2$$

2. Another source of carbon dioxide is in the preparation of hydrogen by passing steam over carbon in the presence of a catalyst (p. 89). The carbon dioxide is separated from the hydrogen by passing the mixture into water under pressure. The carbon dioxide gas is dissolved by the water and is recovered by relieving the pressure on the solution. 3. The gas is also formed in the manufacture of lime (p. 645) and in certain kinds of fermentation (p. 524), and these processes serve as minor sources of the gas. 4. It is obtained directly from certain gas wells, especially in Mexico.

Liquid and Solid Carbon Dioxide · At ordinary temperature (20° C) carbon dioxide is liquefied by a pressure of 56.3 atm. Liquid carbon dioxide is colorless and slightly lighter than water. The liquid dissolves some organic substances but only a few inorganic substances. Commercial carbon dioxide, compressed in steel cylinders, is under such great pressure that it is largely in the liquid state. When the pressure is released, the rapid evaporation of the gas reduces the temperature sufficiently to freeze a portion of the escaping liquid to a snowlike solid.

Under ordinary atmospheric pressure this solid passes directly into a gas, without melting, and sublimes at $-78.5°$. Solid carbon dioxide is

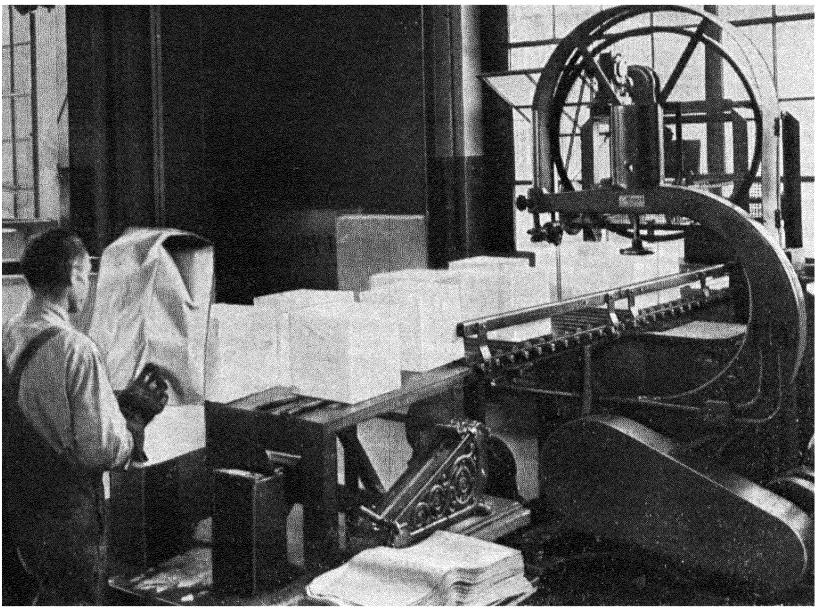


Fig. 27-11. Sawing a Slab of Solid Carbon Dioxide (Dry Ice) into Pieces

now produced on a large scale in nearly all countries, from both natural and artificial sources, for use as a refrigerant.

Physiological Effect of Carbon Dioxide · Carbon dioxide is not regarded as a poisonous gas, but experiments show that one cannot breathe air containing more than 10 per cent of the gas longer than ten minutes without losing consciousness. Air containing 20 per cent or more of the gas causes partial or complete closure of the glottis.

On the other hand, carbon dioxide appears to be the stimulant that acts upon the respiratory nerve centers in breathing; the animal breathes in order to eliminate carbon dioxide. For this reason carbon dioxide is sometimes added to the oxygen (usually about 7 per cent of the dioxide and 93 per cent of oxygen) used in treating cases of lung disorders, asphyxiation, partial drowning, electric shock, and, in general, suspended breathing due to any cause.

Uses of Carbon Dioxide · Commercially, carbon dioxide is used chiefly in the manufacture of soda water and similar beverages, as a fire-extinguisher, and in solid form as a refrigerant. Large amounts are used also in the manufacture of sodium carbonate (p. 294). Ordinary soda water consists of various flavoring extracts, to which is added water charged with carbon dioxide under pressure. When the pressure is removed, some of the gas escapes, producing effervescence.

Solid carbon dioxide under the trade name of "Dry Ice" (Fig. 27-11), has come into favor for the refrigeration of certain foods, especially ice cream. It does not involve the use of sawdust or salt; and it has the advantage of cleanliness, since it evaporates without leaving any residue.

Portable Fire-extinguishers · The flame of a burning candle is extinguished in air containing as little as 2.5 per cent of carbon dioxide; for this reason the dioxide is used as a fire-extinguisher.

Two common types of carbon dioxide fire-extinguishers are shown in Figs. 27-12 and 27-13. That shown in Fig. 27-12 is a device for generating carbon dioxide under pressure. The liquid is a solution of sodium bicarbonate (ordinary baking soda ($NaHCO_3$)) in water contained in a metal cylinder. The bottle, *A*, contains sulfuric acid. In case of fire the apparatus is grasped by the handle, *D*, and inverted. The stopper, *B*, drops on to the support, *C*, thus allowing the acid in the bottle, *A*, to flow out into the solution of sodium bicarbonate. The acid at once reacts with the sodium bicarbonate, generating carbon dioxide, thus:

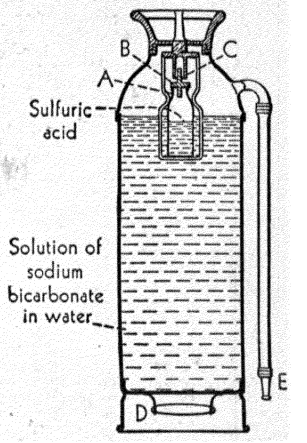
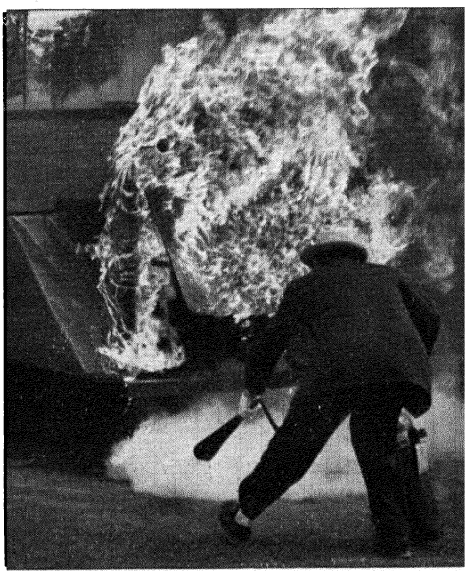


Fig. 27-12. A Fire-extinguisher in Which Water and Carbon Dioxide Are Used to Extinguish Flames

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

The gas forces the water out through the nozzle, *E*. Although the volume of water so obtained is not large, it is very effective as a fire-extinguisher because of the carbon dioxide accompanying it.

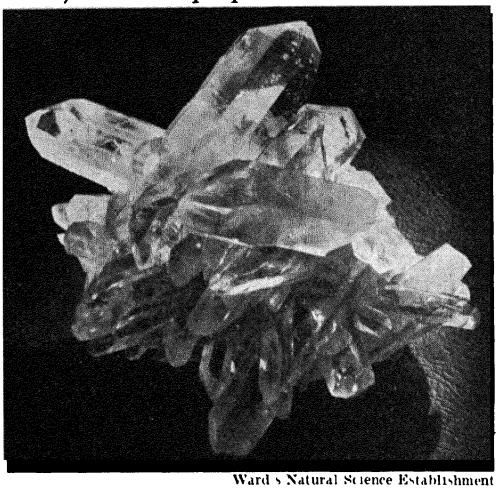
In Fig. 27-13 the carbon dioxide, stored under great pressure, is used directly. When the pressure is removed by turning the valve, a fine spray of gaseous, liquid, and solid carbon dioxide escapes and is directed upon the fire, as shown in the figure.



Walter Kidde and Company, Inc

Fig. 27-13. A Form of Fire-extinguisher A fine spray of gaseous, liquid, and solid carbon dioxide escapes from the metal cylinder, where the gas is stored under great pressure

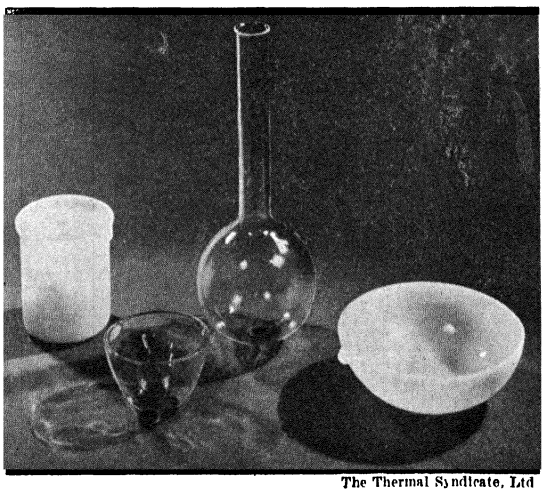
Silicon Dioxide (Silica) (SiO_2) · Although silicon monoxide (SiO), a solid, has been prepared in the electric furnace, the dioxide (SiO_2), called silica, is far better known. Practically all the silicon of nature occurs either as the dioxide itself or as its hydrated derivatives, so that it is a most important substance. The most common crystalline form is that known as quartz (Fig. 27-14). It forms beautiful colorless crystals belonging to the hexagonal system, which are sometimes of great size. A single one found in California weighed over a ton.



Ward's Natural Science Establishment

Fig. 27-14. Quartz Crystals

Quartz crystals, when pure, are colorless. Often small percentages of impurities are present which color the crystals. Some colored varieties are given special names. Thus amethyst is quartz colored violet by a trace of an oxide of manganese, whereas milky quartz owes its characteristic appearance to the minute air bubbles present. Other varieties of silicon dioxide, some of which also contain combined water, are chalcedony, onyx, jasper, opal, agate, and flint. Sand and sandstone are largely silicon dioxide. It is present also in granite and gneiss.



The Thermal Syndicate, Ltd

Fig. 27-15. Laboratory Utensils Made of Fused Quartz

Quartz has a density of 2.65 and is hard enough to scratch glass and most metals. It is therefore used for grinding and polishing purposes. Silica is very difficult to melt, but at the temperature of the oxygen-hydrogen flame (above 1700°) it softens to a viscous liquid resembling melted glass. This can be drawn into threads or fashioned into laboratory utensils (Fig. 27-15).

Such utensils are not attacked by most reagents and, because of the fact that silica has a very small coefficient of expansion with temperature, they can be heated to redness and plunged into water without danger of cracking. Unfortunately quartz vessels are expensive.

Silicosis · There are many industrial operations, such as drilling blast holes and grinding stone objects, in which a dust of silica particles is formed. These particles are very sharp and insoluble. Inhaled into the throat and lungs, dust of this kind results in the serious industrial disease called silicosis.

Varieties of Crystallized Silica · There are three principal crystalline modifications of silica. At about 870° there is a transition point from one variety of quartz (β quartz, Fig. 27-16) into tridymite, and at about 1470° tridymite changes into cristobalite, which is cubic in form. Its crystal lattice is shown in Fig. 27-17. The melting point of silica is therefore the melting point of cristobalite and is given as 1710°. It is very hard to determine with precision, because the melted silica is exceedingly viscous and tends to undercool into a glass. In reality there are two forms of quartz, three of tridymite, and two of cristobalite, making seven forms in all of crystallized silica.

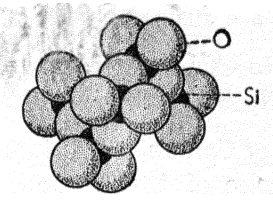


Fig. 27-16. Crystal Lattice of β Quartz

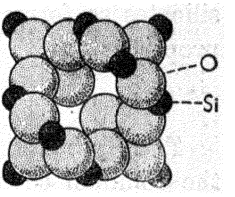


Fig. 27-17. Crystal Lattice of One Form of Cristobalite

Chemical Properties · Carbon dioxide is a very stable substance. At high temperatures partial decomposition takes place, as indicated in the following equation:

$$2\ CO_2 \longrightarrow 2\ CO + O_2$$

At 2000°, under a pressure of 6 atm, about 5 per cent of the carbon dioxide is thus decomposed. It will not combine with oxygen and is therefore incombustible; neither will other substances burn in it under ordinary conditions, for although it contains a large percentage of oxygen, this is held in very firm combination. A few energetic reducing agents remove at least a part of its oxygen. Thus if it is passed over carbon at temperatures above 1000°, the gas is partially reduced, forming carbon monoxide (p. 490). At high temperatures sodium partially reduces carbon dioxide to carbon:

$$3\ CO_2 + 4\ Na \longrightarrow 2\ Na_2CO_3 + C$$

Carbon dioxide is an acid anhydride. When it is dissolved in water, especially under pressure, part of the dissolved gas combines with water according to the equation:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

When the pressure is diminished, the reaction goes in the opposite direction. The product of the reaction, H_2CO_3, is called carbonic acid. It gives the solution a somewhat pungent, or biting, taste.

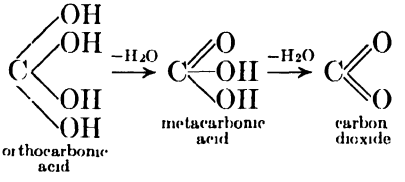
Silica is almost insoluble in water (except when the water is superheated) and in most acids. It is very stable, so that the oxygen which it contains can be removed only by the most powerful reducing agents and at very high temperatures. Hydrofluoric acid attacks it readily. Since it is the anhydride of an acid, it dissolves in fused alkalies to form silicates. Being nonvolatile, it will drive out most other anhydrides when it is heated with their salts to a high temperature, especially when the silicates so formed are fusible. The following equations illustrate this property:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$
$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3$$

The Hydroxides of Carbon and Silicon · Since carbon and silicon have the common covalence of 4, one might expect their hydroxides to be $C(OH)_4$ and $Si(OH)_4$ respectively. One might further expect these hydroxides to be acidic since both carbon and silicon are among the nonmetallic elements. As acids we would write the formulas for these hydroxides H_4CO_4 and H_4SiO_4. These acids, known as *orthocarbonic* and *orthosilicic* acids, are not known and only a few derivatives of orthocarbonic acids are known. There are some salts, however, of orthosilicic acid, such as *garnet*, $Ca_3Al_2(SiO_4)_3$.

Dehydration Products of Orthocarbonic and Orthosilicic Acids · It is often the case among compounds which have more than one hydroxyl group covalently attached to the same atom, that the elements of water are lost and a dehydration product is obtained. This dehydration product is often considerably more stable than the polyhydroxy compound. In the case of orthocarbonic and orthosilicic acids such dehydration is very marked and the contrast between the two is quite striking.

Carbonic Acid · Orthocarbonic acid dehydrates spontaneously to metacarbonic acid, H_2CO_3, and the latter, which is reasonably stable in dilute solution, dehydrates further into the gas, carbon dioxide, and water.

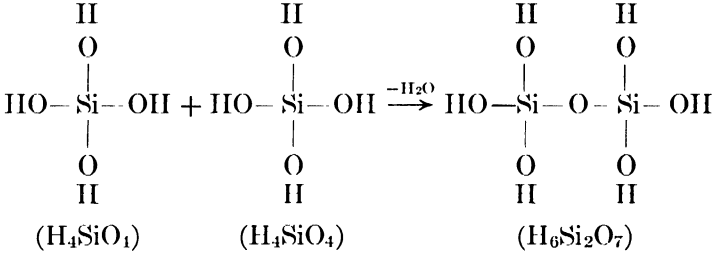


The Silicic Acids · When orthosilic acid is dehydrated, in a process which may take place spontaneously, the dehydration follows a different

course. Since the size of the silicon atom seems to prevent double-bond formation, dehydration takes place between hydroxyl groups attached to *different* silicon atoms, and results in the formation of chains, rings, or a network structure. The resulting acids are called *condensed* acids (see page 419). Attempts to liberate any silicic acid from its salts result in a jellylike substance which, upon heating, is dehydrated continuously to the final, sandlike silica, SiO_2. The equation for this dehydration may be written

$$\underset{\text{orthosilicic acid}}{H_4SiO_4} \xrightarrow{-H_2O} \underset{\text{metasilicic acid}}{H_2SiO_3} \xrightarrow{-H_2O} \underset{\text{silica}}{SiO_2}$$

but it is doubtful if any such simple relationship exists. Instead, since condensation results in chain formation, the products are polysilicic acids. Thus two molecules of orthosilicic acid may unite, with loss of a molecule of water, to form the disilicic acid:



Condensation with a third molecule would yield a trisilicic acid, $H_8Si_3O_{10}$. If condensation proceeded by condensation at the ends of the growing chain, a polysilicic acid of very high molecular weight would be obtained. Chains such as these can, of course, be dehydrated further, and since dehydration always takes place between hydroxyl groups attached to different silicon atoms, the result is a linkage *between chains* (cross-linking). A network structure is produced.

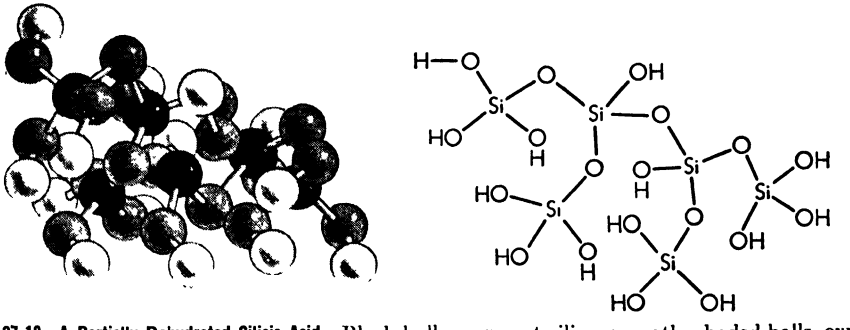


Fig. 27-18. A Partially Dehydrated Silicic Acid · Black balls represent silicon; partly shaded balls, oxygen; colorless balls, hydrogen. Formula, $H_{14}Si_6O_{19}$

Extended indefinitely by further dehydration, a gel-like structure of precipitated silicic acid is formed. Complete dehydration would yield a condensed structure $(SiO_2)_x$ of very high molecular weight. This is the true nature of silica.

Salts of Carbonic and Silicic Acids (the Carbonates and Silicates)

The Carbonates · The salts of carbonic acid are invariably salts of metacarbonic acid, H_2CO_3, usually called simply carbonic acid. They are readily prepared by neutralizing a solution of the acid by a suitable base or by absorbing carbon dioxide, the acid anhydride, in a solution of the base. Since carbonic acid is dibasic, both normal salts and acid salts are known:

$$NaOH + H_2CO_3 \longrightarrow NaHCO_3 + H_2O$$
$$2\,NaOH + H_2CO_3 \longrightarrow Na_2CO_3 + 2\,H_2O$$

1. **Normal carbonates.** The normal carbonates are found in large quantities in nature, and are often used in chemical processes. Some of these are well-known compounds. Ordinary limestone is a more or less impure form of calcium carbonate ($CaCO_3$); marble is nearly pure calcium carbonate in crystalline condition; normal sodium carbonate (Na_2CO_3) is the well-known soda ash, largely used in the manufacture of soap and glass. Among the normal carbonates only those of sodium, potassium, and ammonium are soluble in water, and all the others can be prepared by the general method for preparing insoluble compounds (pp. 451, 628). Since carbonic acid is such a weak acid and is so readily decomposed, almost any acid acts upon a carbonate, with corresponding evolution of carbon dioxide. This reaction is used as a test for carbonates, since the carbon dioxide evolved can readily be detected.

2. **Acid carbonates.** The acid carbonates are made by treating a normal carbonate with an excess of carbonic acid. The most familiar of these is sodium hydrogen carbonate ($NaHCO_3$), or ordinary baking soda. With few exceptions they are unstable and, when heated, readily decompose even in solution. The preparation and properties of the acid carbonates may be illustrated by the following example.

If carbon dioxide is passed into a solution of calcium hydroxide (limewater), calcium carbonate at first precipitates:

$$H_2O + CO_2 \rightleftarrows H_2CO_3$$
$$H_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2\,H_2O$$

If the current of carbon dioxide is continued, however, the precipitated calcium carbonate soon dissolves. This is due to the formation of calcium hydrogen carbonate which, being soluble, dissolves in the water present:

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

If now the solution is heated, the acid carbonate decomposes, and calcium carbonate once more precipitates:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

The Silicates · Since silicic acid is found in the form of various condensed acids, its salts are sometimes quite complex. The natural silicates, which play such an important role in the inorganic world, are found in a variety of structures: fibrous, as in asbestos; platelike, as in mica; and massive, as in meerschaum.

The Structure of the Natural Silicates · In the mineral silicates the SiO_4^{----} grouping of silicon and oxygen atoms plays a dominant role in the crystal lattice. The oxygen atoms are the largest atoms, usually much the largest atoms, present in the lattices. They pack together around the silicon atoms as SiO_4^{----} tetrahedra (Figs. 27-20, 27-21), and the metallic ions fit between the tetrahedra, where they can. X-ray analysis of a large number of silicates shows that there are at least five general types of piling.

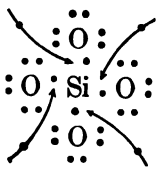


Fig. 27-19. Diagram Representing the Ion SiO_4^{----}

1. **Separate SiO_4^{----} ions.** We should expect the SiO_4 group to carry 4 negative charges because, if the oxygen atoms are bound to the silicon atom by covalent bonds (as we believe they are), 4 extra electrons are needed to complete the stable shells of 8 electrons around every atom (Chap. 20). The silicon atom has 4 valence electrons, and the oxygen atom has 6. When the 4 electrons from the outside are received, the 4 pairs of shared electrons are complete (Fig. 27-19). These 4 electrons, of course, come from metallic atoms (or hydrogen), which, by this act, are *oxidized* to metallic ions, bearing positive charges. These separate ions, SiO_4^{----}, and the metallic ions arrange themselves in various kinds of three-dimensional checkerboard patterns of general resemblance to the Na^+, Cl^- lattice of Fig. 11-28 (p. 187). *Garnet* ($Ca_3Al_2(SiO_4)_3$, or $3\,CaO \cdot Al_2O_3 \cdot 3\,SiO_2$) crystallizes in a lattice of this type.

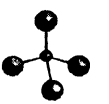
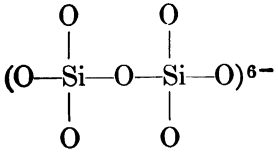


Fig. 27-20. Showing Oxygen Atoms at the Four Corners of a Regular Tetrahedron, and a Silicon Atom at the Center



Fig. 27-21. A Silicate Ion Tetrahedron, Showing Oxygen Atoms to Scale · The silicon atom is buried at the center

2. **Separate, more complex silicon-oxygen ions.** The ion $(Si_2O_7)^{6-}$ is formed when two silicon atoms share the same oxygen atom between them:



A *ring*-shaped ion, $(Si_6O_{18})^{12-}$, is also known (Fig. 27-20). Such complex negative ions as these, together with metallic ions, make up the crystal lattice. The ring ion of Fig. 27-22 is present in the lattice of *beryl* ($Be_3Al_2Si_6O_{18}$, or 3 Be^{++}, 2 Al^{+++}, $(Si_6O_{18})^{12-}$).

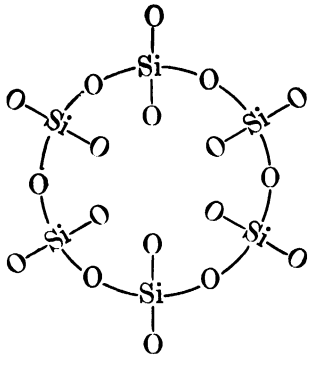
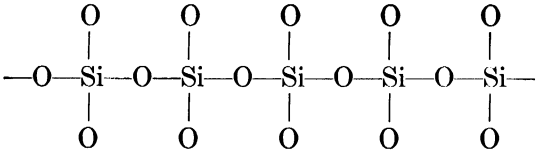
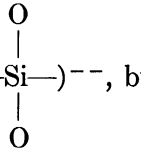


Fig. 27-22. Structural Formula of $(Si_6O_{18})^{12-}$

3. **Silicon-oxygen strings (one-dimensional).** Silicon-oxygen strings are common:



Actually the strings are zigzag, as shown in the picture of the lattice of β quartz (Fig. 27-16). Strings of this kind, or of a closely related kind, occur in all the fibrous silicates —for instance, in *tremolite*, a form of asbestos, $CaMg_3(SiO_3)_4$. These strings are extremely long and may run from one end of the crystal fiber to the other. They are held together laterally by metallic ions. (Fig. 27-23).

The SiO_3 groups bear 2 negative charges,  , but they do not form separate ions along the string. Fig. 27-23 represents merely a short section of such a string.

4. **Silicon-oxygen sheets (two-dimensional).** The silicon and oxygen atoms also crystallize in *sheets* (Fig. 27-24), which are held together by positive ions located between the sheets. All the micas have this style of lattice—for example, *muscovite* ($H_2KAl_3(SiO_4)_3$).

5. **Silicon-oxygen nets (three-dimensional).** Finally the silicon and oxygen atoms often crystallize in a continuous three-dimensional network, with the metallic ions fitting into the holes. Many examples of this type are found among the feldspars—for instance, *albite* ($NaAlSi_3O_8$).

Silicates in Solution · The ions in silicate crystals are usually bound together by very strong forces, with the result that the melting points of the silicates are nearly always rather high, and very few of the silicates are soluble in water. Among these few are sodium and potassium silicates. Sodium silicate may be prepared by fusing pure silica with sodium hydroxide or carbonate:

$$4\,NaOH + SiO_2 \longrightarrow Na_4SiO_4 + 2\,H_2O$$
$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

A solution of the products of such fusions in water is called *water glass*. It consists of a mixture of various silicates of sodium. When the solution is evaporated, it forms a thick liquid, which gradually hardens into a glass. Sodium silicate can be obtained also in a crystalline condition. It has many uses, especially as an ingredient of soap, as a protective coating for porous surfaces (such as those of wood, plaster, or cement), and as a cement or glue, chiefly for pasteboard boxes and cartons.

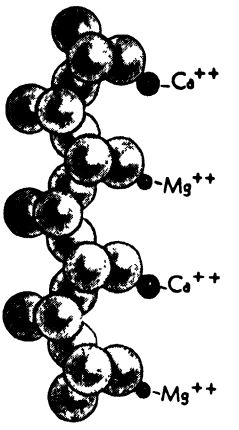


Fig. 27-23. Silicon-Oxygen String in Asbestos · Silicon atoms are buried at the center of the oxygen tetrahedron

When salts of the various metals are added to a solution of a sodium silicate, such as Na_2SiO_3, insoluble silicates are precipitated:

$$Na_2SiO_3 + CaCl_2 \longrightarrow CaSiO_3\downarrow + 2\,NaCl$$

Most natural silicates, when fused with sodium carbonate, are decomposed, and sodium silicate is formed:

$$CaSiO_3 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SiO_3$$

The melted sodium carbonate forms a liquid, in which the silicates are soluble but the carbonates are not. The insoluble carbonate is therefore precipitated. When the melt is cooled and digested with water, the sodium silicate dissolves, while the carbonate and oxides of the other metals are left undissolved. They may be filtered off and dissolved in acids. Such fusions are very frequently resorted to in chemical analysis as a means of decomposing the silicates and getting their constituents into solution, since many of them are not attacked by acids.

Fusion of the Silicates · Some of the silicates have sharp melting points and recrystallize on cooling. Many of those with relatively low melting points resemble silica in that they fuse into viscous liquids which, on cooling, harden without crystallizing. If several different silicates are melted together with an excess of silica, they mix freely to a homogeneous liquid. Crystals may separate from the melt when it is cooled, but usually

the liquid solution simply becomes more and more viscous until it is as rigid as a true solid. Such products are called *glasses*, and they may be regarded as very viscous solutions of one silicate in another or in silica. Extensive silica lattices do not crystallize in glasses, because the positively charged ions get in the way.

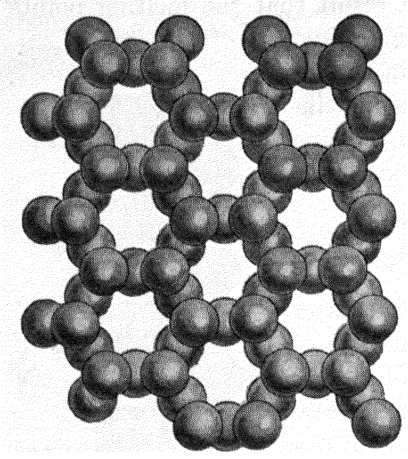
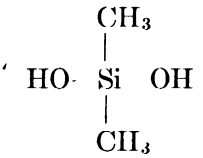


Fig. 27-24. Silicon-Oxygen Sheet in Mica Showing Arrangement of the Oxygen Atoms Only

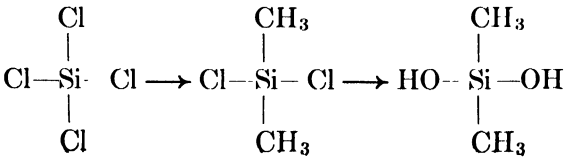
The Ceramic Industries · A number of most important industries are based upon the silicates and the chemical transformations which they undergo. The oldest of these are the various ceramic industries, including the making of bricks, tile, terra cotta, dishes, porcelain, and glass. Chapter 45 will be devoted to this topic.

Silicones · Most silicates have a certain amount of linkage in all four directions from the silicon atom. It is this cross-linking, resulting from the fact that silicic acid is tetrafunctional (with four reactive hydroxyl groups), which leads to the great rigidity of the silicates. If one could block off two of the reactive positions so that the silicic acid became bifunctional, dehydration could only lead to chains (or, possibly, rings). The cross-linking between chains would be absent. Such molecules, while they may be large, are threadlike, and can still move past each other. Materials made up of such molecules are less brittle because they can yield somewhat to a strain, but are still tough.

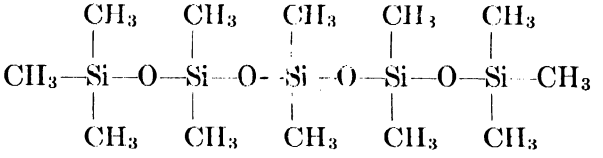
This blocking is accomplished in the case of silicic acid by preparing the compound dimethyl silicon dihydroxide



This compound is prepared by replacing two chlorine atoms in $SiCl_4$ with methyl groups and hydrolyzing the remaining chlorine atoms



Dimethyl silicon dihydroxide dehydrates normally to form a chain. Such a compound is called a *silicone*; and this particular one is a methyl silicone. Other groups, like the ethyl group, C_2H_5, may be substituted for the methyl group; and the molecule chain can be made in various lengths. By including small amounts of the monofunctional $(CH_3)_3SiCl$ along with the bifunctional $(CH_3)_2SiCl_2$, a short methyl silicone molecule may be made. It is represented by the following graphical formula, which shows the bonds of the silicon and oxygen atoms:



Properties and Uses of the Silicones · Some of the methyl silicones are oily liquids, and they become more viscous as the chain length increases. They are used as lubricants, either incorporated in greases or as oils, in bearings, gears, etc., and they are used in hydraulic brakes and other hydraulic systems. The outstanding physical attribute of silicone oil is its very small change in viscosity with change in temperature, compared with the behavior of other oils of like viscosity. If the temperature is dropped from 100° F to 0° F, the viscosity of a petroleum oil may increase about one hundred fold, whereas that of silicone oil will increase less than fourfold. In the presence of air or oxygen at temperatures as high as 300° F, silicone oils remain free from discoloration, acid formation, sludging, oxidation, and similar phenomena, which frequently limit the usefulness of petroleum products and synthetic organic liquids. In the absence of air or oxygen—for example, in a sealed or evacuated system—silicone oils are stable at temperatures well over 400° F.

Methyl silicones of high molecular weight resemble rubber, and are made into rubber-like tubing and sheets. Silicone molecules can be made in such a way that bridges, or cross-linkages, bind one long molecule to another at several points along the chain. Then the body has *resinous* properties, and has an extensive use in electrical insulation.

Another interesting and important application of silicones is their use in the treatment of various surfaces to make them water-repellent. If the material to be treated is exposed to the vapor of methylchlorosilane, reaction occurs with water on the surface, and hydrogen chloride splits out, as in the reaction previously described. A silicone film, adhering lightly to the material, then covers the surface, paves it effectively with methyl groups, and repels water in much the same way that a film of

grease would. (See the discussion of solubility, page 190.) Much of the leak of electricity through the moisture film on ceramic electrical insulators can be prevented by a silicone film; and cloth, plastics, asbestos, glass, leather, and paper, even filter paper and blotting paper, become strongly water-repellent when covered with a silicone film.

The silicone industry is in rapid development, and evidently has an important future.

QUESTIONS

1. From their positions in the periodic table, state what properties you would expect the elements carbon and silicon to have, particularly with reference to (*a*) valence, (*b*) metallic or nonmetallic character, and (*c*) bond types in their compounds.

2. (*a*) What properties of a solid might be predicted from a knowledge of its crystal structure? (*b*) What is the unit particle in a crystal of (1) sodium chloride? (2) carbon dioxide? (3) silicon dioxide? (4) diamond? (5) graphite?

3. How can you account for the fact that (*a*) a diamond is hard while graphite is relatively soft? (*b*) carbon dioxide is a gas while silicon dioxide is a high-melting solid? (*c*) carbonic acid when liberated decomposes rapidly with liberation of a gas, while silicic acid when liberated rapidly forms a gel?

4. (*a*) How do you explain the presence of carbon monoxide in the combustion products of gas stoves and automobile engines? (*b*) How could the carbon monoxide content in these products be reduced? (*c*) Why is carbon monoxide considered to be such a dangerous gas?

5. (*a*) Should you expect the reaction between hydrochloric acid and marble to be complete? (*b*) Why? (*c*) Would a solution of sodium carbonate be acid, basic, or neutral? (*d*) Why? (*e*) Should you expect all carbonates to undergo hydrolysis? (*f*) Should you expect all carbonates to react with any acid?

6. The carbonates and sulfites have similar formulas and similar solubilities. In what other respects are they similar?

7. A solution of sodium silicate must be kept basic in order to prevent formation of a gel. How do you explain this fact?

8. What is the role of carbon dioxide in photosynthesis?

9. Complete and balance the following equations:

a. $C + H_2O \xrightarrow{\text{heat}}$

b. $CO + O_2 \longrightarrow$

c. $Ca(OH)_2 + CO_2 \longrightarrow$

d. $OH^- + CO_2 \longrightarrow$

e. $CaCO_3 + CO_2 + H_2O$

f. $CaCO_3 + H^+ + CO_3^{--} \longrightarrow$

g. $Ca(HCO_3)_2 \xrightarrow{\text{heat}}$

h. $CO + Fe_2O_3 \longrightarrow$

i. $Na_2SiO_3 + H^+ \longrightarrow$

j. $SiO_2 + H_2F_2 \longrightarrow$

PROBLEMS

1. On analysis a compound gave the following results: carbon, 15.8 per cent; sulfur, 42.1 per cent; nitrogen, 36.8 per cent; hydrogen, 5.3 per cent. (*a*) Calculate the simplest formula for the compound. (*b*) Nineteen grams of the compound, dissolved in 1 liter of water, lowered the freezing point of the water 0.4675°. What is the molecular weight of the compound?

2. What volume of carbon monoxide will be required for the synthesis of 40 g of carbonyl chloride?

3. What volume of carbon dioxide under standard conditions can be produced from 200 g of carbon?

4. What volume of carbon dioxide under standard conditions can be obtained by heating gently 500 g of calcium hydrogen carbonate?

5. (*a*) What weight of carbon monoxide must be burned in order to produce 102,000 cal? (*b*) What volume will this amount of carbon monoxide occupy under 700 mm and at 26°?

6. What weight of carbon dioxide is necessary in order to change the base present in 500 ml of 0.4 *N* NaOH to sodium carbonate?

7. What per cent of aluminum is there in a clay whose average composition is represented by the formula

$$Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O?$$

CHAPTER 28

INTRODUCTION TO ORGANIC CHEMISTRY: THE HYDROCARBONS

Historical. In the early days of the science, more than one hundred years ago, chemists believed that the organic compounds of carbon were to be found only in living organisms. It was supposed that these compounds could be formed only through the influence of the living, or vital, force of organisms, and that it would be impossible to prepare them in the laboratory by synthetic methods. In 1828 the German chemist Wöhler, in the course of some experiments with an inorganic compound, ammonium cyanate, chanced to prepare from it a white crystalline compound which, much to his surprise, proved to be *urea*, a typical organic compound, previously known only as a product of life processes.

It was not long before other compounds found in living organisms were synthesized in the laboratory from purely inorganic material, and the old belief was gradually abandoned. The term *organic chemistry* was retained as the name of the chemistry of all carbon compounds; it includes the chemistry of most of the compounds found in living organisms, not because they are found in these organisms, but because they contain carbon.

General · A few well-known organic compounds are acetylene, acetone, Bakelite and Nylon and other high polymers, benzene, cellulose, fats, formaldehyde, glycerin and nitroglycerin, insulin and egg albumin and other proteins, octane, rubber, starch, sugar, and vitamins.

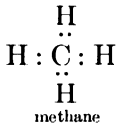
The compounds of carbon are far more numerous than those of any other element. Some 30,000 carbon compounds have been identified in nature; some 600,000 others have been synthesized by chemists in their laboratories; and the number theoretically possible is without limit.

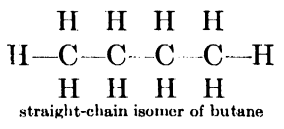
Reasons for the Existence of So Many Compounds of Carbon · The explanation of the fact that there are so many carbon compounds lies in the nature of the carbon atom. (1) Carbon atoms form strong, stable covalent bonds with other carbon atoms, as well as with hydrogen, oxygen, and some other atoms; (2) they are tetravalent, and have the ability to unite with other carbon atoms to form chains and rings; and (3) they can form *isomers*. Isomers are compounds with the same number and kind of atoms but differently arranged.

We can illustrate these properties of the carbon atom with the molecules of the following familiar organic compounds:

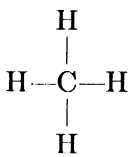
methane, CH_4, found in natural gas
butane, C_4H_{10}, present in "bottled" gas
benzene, C_6H_6, found in coal tar
naphthalene, $C_{10}H_8$, used to make moth balls

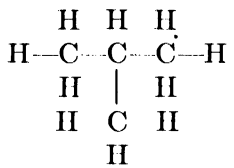
The formulas for these compounds may be written by showing the valence electrons, or, as is the more usual practice of organic chemists, by using the single line (—), a valence bond, to represent a shared pair of electrons. Such formulas are called structural formulas:

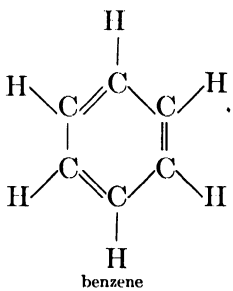

methane

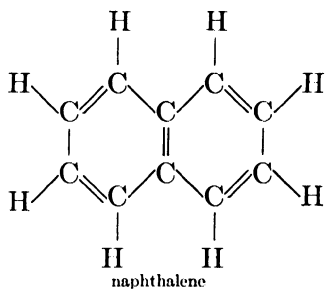

straight-chain isomer of butane

or


methane


branched-chain isomer of butane


benzene


naphthalene

The covalent character of carbon is illustrated in the electronic formula for methane. With but few exceptions (for example, in carbon monoxide) carbon is tetravalent, sharing four pairs of electrons.

In many compounds two carbon atoms share two pairs of electrons. This is indicated by two lines in the structural formula, and is called a *double* bond; the formulas for benzene and naphthalene contain double bonds. Later we shall learn how three pairs of electrons can be shared by two carbon atoms, giving a triple bond (p. 517).

That carbon atoms can form chains is shown by the formulas for butane. These chains may be "straight" (that is, unbranched), as in the

upper formula, or branched, as in the lower; and this makes it possible to have isomers (p. 508). The chains are like the chains of carbon atoms in the crystal lattice of diamond (Fig. 27-1, p. 484), and can be of various lengths. Compounds of carbon and hydrogen, whose molecules contain as many as 60 carbon atoms, are known.

Carbon atoms also form into rings, as illustrated by the formulas for benzene and naphthalene. Such structures resemble the single, double, and multiple rings to be found in the crystal lattice of graphite (Fig. 27-2, p. 485).

Structural Formulas; Molecular Architecture · The organic chemist for the most part makes use of the *structural* formula, which shows how the atoms are arranged within the molecule and joined to one another; whereas *molecular* formulas, such as CH_4 (methane), C_4H_{10} (butane), C_6H_6 (benzene), or $C_{10}H_8$ (naphthalene), show merely the kinds and numbers of atoms present in the molecule.

Sometimes *condensed*, or *semistructural*, formulas are used, in which the chain of carbon atoms is indicated along with the atoms attached to them. For example, for the butanes we should have $CH_3—CH_2—CH_2—CH_3$ and

$$CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}—CH_3$$

The varied patterns of structure of the organic molecules suggest the term *molecular architecture*; and we should point out that the chains and rings that we have been describing are basic elements in this architecture. These chains and rings, once hydrogen atoms are attached to their free bonds, give rise to a great variety of molecules—hydrocarbon molecules. But more than that, they serve as the skeletons upon which other groups of atoms, often containing oxygen, are built. These groups, called *functional* groups, may be attached to the skeleton molecule at various points; and naturally such a varied pattern of attachment of different groups increases enormously the number of possible molecular structures.

Families of Carbon Compounds; Functional Groups · The existence of such a large number of carbon compounds presents a tremendous problem to the student who wishes to learn about them. However, the problem may be simplified by grouping the compounds into families. Within a family there are similar properties, resulting from the similarity of structure of the compounds belonging to that family. A family is characterized by the presence in its molecules of certain reactive groups such as $—\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}—H$ (in aldehydes) or $—\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}—OH$ (in acids), two of the charac-

teristic or so-called *functional* groups. There are about a dozen such groups that are important to us.

Indeed, since in most reactions the carbon chain or ring remains unchanged when the functional groups react, it is convenient to consider all organic compounds which are built up on the hydrocarbon skeleton to be derivatives of the hydrocarbons. The carbon *chains* are the skeletons upon which the so-called *aliphatic* molecules are built; and the *ring* structures of the graphite type are the skeletons of the *aromatic* compounds. In this chapter we shall now consider the aliphatic hydrocarbons; in later chapters we shall learn about the aromatic compounds and some of the various functional groups.

Hydrocarbons, the Parent Substances of Aliphatic Compounds · The aliphatic hydrocarbons—those having straight or branched chains—are obtained chiefly from petroleum and natural gas, but many have been made synthetically. Some of the important compounds (all having straight chains) found in petroleum and natural gas are listed in the following table:

SOME ALIPHATIC HYDROCARBONS FOUND IN PETROLEUM AND NATURAL GAS

FORMULA	CHEMICAL NAME	PHYSICAL STATE	BOILING POINT*	COMMON NAME
CH_4	Methane	Gas	− 161°	Natural gas
C_2H_6	Ethane	Gas	− 88°	
C_3H_8	Propane	Gas	− 46°	
C_4H_{10}	Butane	Gas	− 1°	
C_5H_{12}	Pentane	Liquid	36°	High-grade naphtha
C_6H_{14}	Hexane	Liquid	69°	
C_7H_{16}	Heptane	Liquid	98°	Gasoline
C_8H_{18}	Octane	Liquid	126°	
C_9H_{20}	Nonane	Liquid	150°	
$C_{10}H_{22}$	Decane	Liquid	174°	
$C_{11}H_{24}$	Undecane	Liquid	195°	
$C_{12}H_{26}$	Dodecane	Liquid	215°	Kerosene ($C_{12}H_{26}$ to $C_{18}H_{38}$)
$C_{13}H_{28}$	Tridecane	Liquid	234°	
$C_{14}H_{30}$	Tetradecane	Liquid	253°	Lubricating oil (mixtures of higher hydrocarbons)
$C_{15}H_{32}$	Pentadecane	Liquid	271°	
$C_{20}H_{42}$	Eicosane	Solid	—	Paraffin ($C_{20}H_{42}$ to $C_{30}H_{62}$)
$C_{60}H_{122}$	Hexecontane	Solid	—	

*The data given here are for the normal, or straight-chain, hydrocarbons.

These compounds are obtained in the process of fractional distillation of petroleum.

A study of the table will show that each member of the series (through $C_{15}H_{32}$) differs from the one preceding it by the group of

atoms CH_2. Any such series of organic compounds is called a *homologous series*. The one shown in the table is named the *methane series of hydrocarbons*, after its simplest member; and sometimes it is called the *paraffin* series (p. 515). The members of the methane series have the general formula C_nH_{2n+2}, in which n stands for the number of carbon atoms. The members of any homologous series are similar in their chemical properties, and show a regular gradation in some of their physical properties.

Physical Properties of the Hydrocarbons of the Methane Series · In the homologous series of hydrocarbons whose first member is methane, the boiling points of the hydrocarbons gradually increase with each added CH_2 group. The lower members of the series are gaseous (natural

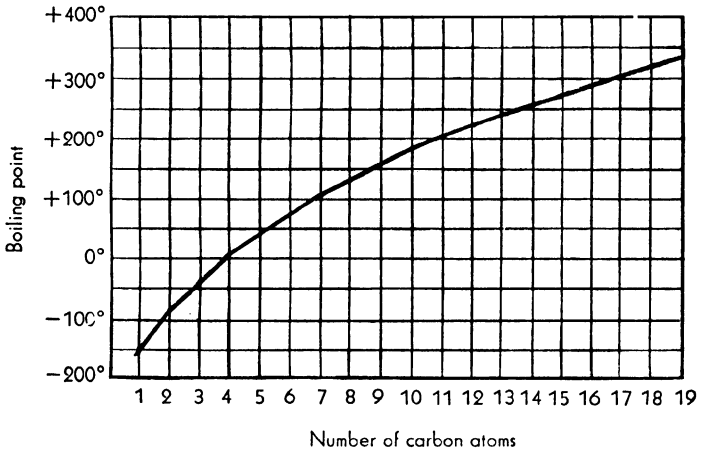


Fig. 28-1. The Boiling Points of the Normal Paraffin Hydrocarbons CH_4 to $C_{19}H_{40}$

gas), the members of intermediate molecular weight are liquids (gasoline, kerosene, and lubricating oil), while the higher members are solids.

The branched-chain compounds usually boil at a slightly lower temperature than the *normal* (straight chain) compounds of the same number of carbon atoms. Hydrocarbons are insoluble in water but soluble in certain organic liquids, such as ether and benzene.

Methane · The simplest hydrocarbon is methane (CH_4), with the four hydrogen atoms attached by covalent bonds to the carbon atom (p. 509). The four valence bonds about a carbon atom are oriented in such a way as to be as far apart as possible, as shown in the model of a methane molecule, where the valence bonds radiate to the atoms in the four corners of a regular tetrahedron (Fig. 30-5, p. 547). The angle formed between any two of these valence bonds is a *tetrahedral angle*, about $109\frac{1}{2}°$.

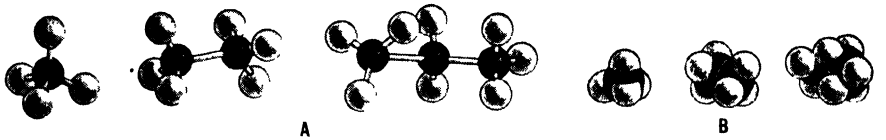
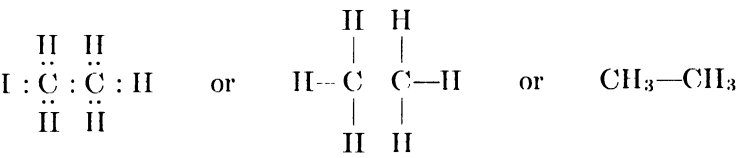


Fig. 28-2. Two Types of Models, A and B, Showing the Structures of Methane, Ethane, and Propane · *A*, space models showing bond angles; *B*, space models showing distances between atoms and sizes of atoms · to scale · sometimes called scaled models

Methane is the chief constituent of natural gas. It is formed in marshes by the decay of vegetable matter under water, and bubbles of the gas are often seen to rise when the dead leaves on the bottom of a pool are stirred. It also collects in mines and, when mixed with air, is called *fire damp* by the miners because of its great inflammability. (*Damp* is an obsolete name for a vapor or a gas.) It is formed when organic matter, such as coal or wood, is heated in closed vessels, and is therefore a principal constituent of ordinary coal gas.

Ethane · The second member of the methane series is ethane (C_2H_6):



The structure of the molecule of ethane may be understood if we assume two carbon atoms to be united, and thus one valence bond of each satisfied; the remaining three valences of each carbon atom are then satisfied by union with hydrogen atoms.

Butanes; a Pair of Isomers · There are two hydrocarbons of the formula C_4H_{10}; they are isomers, having the same molecular formula but different structural formulas (Fig. 28-3).

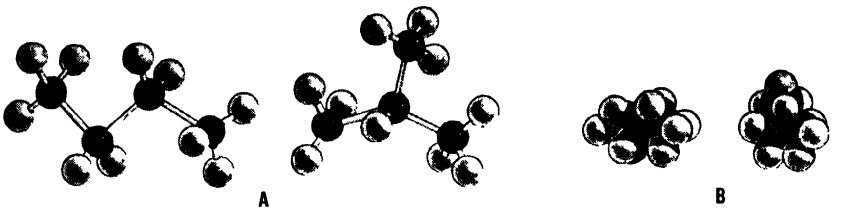
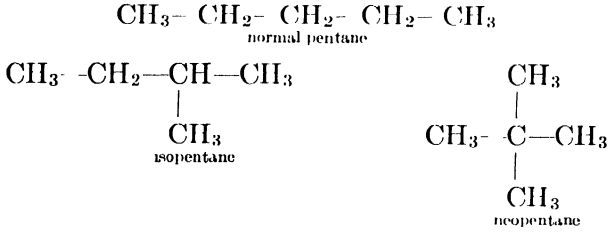


Fig. 28-3. Two Types of Models, A (Space Models) and B (Scaled Models), Showing the Structures of Butane and Isobutane

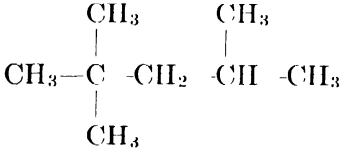
The butanes are gases at ordinary temperatures, and can be compressed or liquefied and stored in metal containers. Butane and propane (C_3H_8) are used as fuels in many parts of the country where natural gas is not readily available. They are sometimes called "bottled" gas.

Isomers of hydrocarbons · Three hydrocarbons of the formula C_5H_{12} are theoretically possible if every carbon atom maintains its covalence of 4:



There are five hydrocarbons with the formula C_6H_{14} (hexane), nine with C_7H_{16} (heptane), and 802 possible compounds with the formula $C_{13}H_{28}$. In general, as the number of carbon atoms increases, the number of isomers increases rapidly. The existence of isomers is one of the reasons for the large number of carbon compounds.

Octanes (C_8H_{18}) · There are eighteen possible isomers of octane. One of its very important isomers has the formula:



This particular isomer is called *iso-octane*. It is used to make high-test gasoline, and also in testing antiknock value (p. 597).

Naming the Hydrocarbons · The simpler members of the methane series have common names, such as methane, ethane, propane, and butane. The names of hydrocarbon derivatives are derived from these names. Thus the compound CH_3Cl is *methyl* chloride, and the CH_3- group is the methyl group; it is methane, CH_4, minus one hydrogen atom. Such a fragment of a molecule is known as a *radical*. It has an independent existence only momentarily, since it quickly combines, on its free bond, with something else. Other examples are the *ethyl* and *propyl* radicals, C_2H_5- and C_3H_7- (ethane and propane, respectively, minus a hydrogen atom).

Radicals derived from any of the hydrocarbons of the methane series are called *alkyl groups*; and the chemist often uses the symbol R to represent them.

Isomers are sometimes distinguished from each other, as already intimated, by the word *normal* and the prefix *iso*. The removal of a hydrogen atom from a molecule of propane results in the formation of either

of two radicals, either *normal* propyl, $CH_3—CH_2—CH_2—$, or *iso*-propyl, $CH_3—\underset{|}{CH}—CH_3$, also written $CH_3—\underset{|}{CH}—$. As the number of carbon
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3$
atoms and possibilities for branching increases, these simple names will no longer suffice to describe the compound exactly, and a more complex system of nomenclature must be used.

Chemical Properties of the Hydrocarbons of the Methane Series · In their chemical properties these hydrocarbons are characterized by their inertness toward most reagents; hence the name *paraffin* (from the Latin *parum*, "too little," and *affinis*, "akin"). Two of the important reactions which they undergo are those with oxygen and chlorine.

1. **Reaction with oxygen.** At high temperatures these hydrocarbons burn, and this, of course, is the reason for their use as fuels. Carbon dioxide and water are the sole products of complete combustion. Typical reactions are

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$
$$2\,C_6H_{14} + 19\,O_2 \longrightarrow 12\,CO_2 + 14\,H_2O$$

2. **Reaction with chlorine (substitution).** With chlorine these hydrocarbons react by the substitution of chlorine for hydrogen. Methane, for example, in the presence of sunlight, may be chlorinated to form four different compounds as follows:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$
$$CH_4 + 2\,Cl_2 \longrightarrow CH_2Cl_2 + 2\,HCl$$
$$CH_4 + 3\,Cl_2 \longrightarrow CHCl_3 + 3\,HCl$$
$$CH_4 + 4\,Cl_2 \longrightarrow CCl_4 + 4\,HCl$$

Halogen Substitution Products of the Paraffins. 1. **Products of the halogenation of methane.** Methyl chloride (CH_3Cl) is a sweet-smelling gas, easily liquefied. Chloroform, or trichloromethane ($CHCl_3$), is the well-known anesthetic. It is a heavy liquid, relatively insoluble in water, and has a sweet odor. Carbon tetrachloride, or tetrachloromethane (CCl_4), is also a heavy liquid, insoluble in water. It is noncombustible and has been used as a fire-extinguisher under the name "Pyrene." Carbon tetrachloride is an excellent solvent for fats and greases and is used largely as a dry-cleaning agent. Dichlorodifluoromethane (CCl_2F_2), or Freon, is a widely used refrigerant (p. 177).

2. **Products of the halogenation of ethane; position isomers.** The chlorination of ethane yields a variety of products, of which ethyl chloride (monochloroethane) is the simplest:

$$CH_3—CH_3 + Cl_2 \longrightarrow CH_3—CH_2Cl + HCl$$

When two of the hydrogen atoms of ethane are replaced by two chlorine atoms, there are two possible products. Both of the replaced hydrogen atoms may have been attached to the same carbon atom, or one attached to one carbon atom and one to the other. (See the models in Fig. 28-4).

CH_3-CHCl_2	CH_2Cl-CH_2Cl
ethylidene chloride, or 1, 1-dichloroethane	ethylene dichloride, or 1, 2-dichloroethane

Hence two isomers of $C_2H_4Cl_2$ are known. They are said to be *position isomers*, since they differ in the position of a substituent (chlorine) along the hydrocarbon chain. As the molecular weight of the hydrocarbon increases, the possibility of this kind of isomerism also increases. In

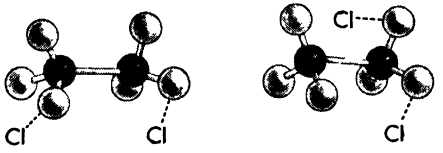


Fig. 28-4. Models Showing the Structures of the Two Isomeric Dichloroethanes

propane, $CH_3-CH_2-CH_3$, two position isomers are possible with only one substituent:

$$CH_3-CH_2-CH_2X \text{ and } CH_3-CHX-CH_3$$

3. **General properties and use of halogenated hydrocarbons.** The halogenated paraffins are characterized by their high density, relative inertness, and noninflammability. One important use for them in recent years has been for fireproofing fabrics.

The halogenated hydrocarbons have played a very important role in the development of organic chemistry, since they undergo a variety of reactions, leading to the formation of many types of organic compounds. Some of these reactions will be discussed later.

Preparation of Hydrocarbons · Methane is prepared in the laboratory by heating sodium acetate with sodium hydroxide (or with a mixture of sodium and calcium hydroxides known as soda lime):

$$NaC_2H_3O_2 + NaOH \longrightarrow Na_2CO_3 + CH_4$$

It can be prepared also by the action of water on aluminum carbide:

$$Al_4C_3 + 12\ H_2O \longrightarrow 4\ Al(OH)_3 + 3\ CH_4$$

Ethane and the higher homologues of methane may be prepared by a variety of processes, one of which is the Wurtz synthesis. In this reaction an alkyl halide or a mixture of alkyl halides is treated with metallic sodium, with the formation of hydrocarbons of higher molecular weight

Hydrocarbons with Double and Triple Bonds · Many carbon compounds are known which contain *double* or *triple* bonds between the carbon atoms, as in ethylene, $H_2C{=}CH_2$, and in acetylene, $HC{\equiv}CH$. Such compounds are said to be *unsaturated*, since they are able to take on other atoms or groups of atoms at their double or triple bonds.



Fig. 28-5. Models Showing the Structures of Fthylene and Acetylene

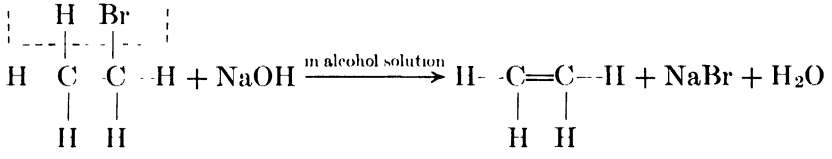
Two common series of unsaturated hydrocarbons are

ETHYLENE SERIES	ACETYLENE SERIES
$H_2C{=}CH_2$	$HC{\equiv}CH$
$CH_3HC{=}CH_2$	$CH_3C{\equiv}CH$
$CH_3CH_2HC{=}CH_2$	$CH_3CH_2C{\equiv}CH$
$CH_3CH_2CH_2HC{=}CH_2$	$CH_3CH_2CH_2C{\equiv}CH$
(Formula, C_nH_{2n})	(Formula, C_nH_{2n-2})

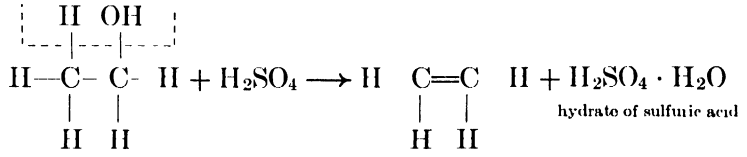
The first four members of each series are shown in semistructural formulas. The members of the ethylene series are referred to as *ethylene* (C_2H_4), *propylene* (C_3H_6), *butylene* (C_4H_8), and *amylene* (C_5H_{10}).

Formation and Preparation of Hydrocarbons of the Ethylene Series · 1. **Laboratory method.** In the laboratory there are two rather easy methods of producing hydrocarbons of the ethylene series.

a. The removal of hydrogen bromide (or some other hydrogen halide) may be accomplished with sodium hydroxide:



b. The dehydration of ethyl alcohol gives ethylene:



In the laboratory sulfuric acid is used as the dehydrating agent.

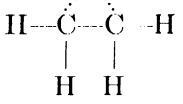
2. **Industrial method.** In industry many double-bonded compounds are formed when petroleum is "cracked." In the "cracking" process the large molecules, such as those found in kerosene and light oils (fuel oil),

for which there is little commercial use, are broken down by catalysts or by heat under high pressure to smaller ones; for example:

$$\text{Light oil containing } C_{16}H_{34} \xrightarrow[\text{pressure}]{\text{heat}} \underset{\substack{\text{saturated}\\(\text{formula, } C_nH_{2n+2})}}{C_8H_{18}} + \underset{\substack{\text{unsaturated}\\(\text{formula, } C_nH_{2n})}}{C_8H_{16}}$$

This is an important type of reaction in making gasoline.

Properties of Compounds with Double Bonds · In their physical properties, such as boiling point, freezing point, and specific gravity, these hydrocarbons resemble the methane hydrocarbons which have the same number of carbon atoms. In their chemical reactions, however, they show a marked difference. Not only are they much more reactive, but they react with most reagents *by addition* at the double bond. This can be illustrated, with the molecule of ethylene, by writing the expanded structural formula as though each of the two carbon atoms had an unsatisfied valence bond.



Ethylene adds other atoms or groups in the following manner:

$$CH_2{=}CH_2 + H_2 \xrightarrow{\text{catalyst}} CH_3{-}CH_3$$

$$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2Cl{-}CH_2Cl$$

$$CH_2{=}CH_2 + HCl \longrightarrow CH_3\ \ CH_2Cl$$

$$CH_2{=}CH_2 + HOH \xrightarrow{\text{catalyst}} CH_3\ \ CH_2OH$$

Note that in each addition one atom or group is joined to one of the carbon atoms, and one atom or group to the other carbon atom, and there are no by-products. The compounds formed by the addition reactions contain no unsatisfied valences and are said to be saturated; correspondingly the double-bonded (and triple-bonded) compounds, which are capable of undergoing addition reactions are said to be unsaturated.

Ethylene (C_2H_4) · The simplest and most important of the members of this series of unsaturated hydrocarbons is ethylene. It is a colorless, inflammable gas.

Ethylene is used (1) as a fuel, (2) as an agent for speeding up the ripening of citrus fruits, (3) in the manufacture of ethylene dibromide, (4) as an anesthetic in surgical operations, and (5) as an intermediate in the production of many important organic compounds, such as alcohol and certain plastics (Chap. 32).

Compounds with More than One Double Bond · Organic compounds may have more than one double bond; a well-known compound of this

type is butadiene (C_4H_6), which is used in making synthetic rubber. Its structural formula is $CH_2{=}CH{-}CH{=}CH_2$. Compounds which have two double bonds separated by one single bond are said to have *conjugated* double bonds. Molecules of this kind have a pronounced tendency to react with themselves or with other similar molecules to form long, thread-like molecules called linear or chain polymers (Chap. 32).

Acetylene, a Compound Containing a Triple Bond · The simplest and most important compound with a triple bond (p. 517) is acetylene ($HC{\equiv}CH$). It is a colorless gas. The easiest, as well as the most economical, method for its preparation involves the action of water upon calcium carbide:

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

Acetylene, when pure, has a faint, rather pleasant odor. As ordinarily prepared, however, it has a disagreeable odor, due to impurities. It can be condensed to a liquid boiling at $-83.6°$.

Acetylene, with the proper admixture of air, burns with a brilliant white light. The flame is very hot when the gas is burned in oxygen:

$$2\ C_2H_2 + 5\ O_2 \longrightarrow 4\ CO_2 + 2\ H_2O + 2 \times 312{,}000\ \text{cal}$$

This is the reaction that takes place in the oxyacetylene blow torch (p. 589).

Acetylene is very explosive when subjected to pressure, but it can be compressed with safety by forcing it at low temperatures into metal cylinders completely filled with some porous material which has been partially saturated with certain liquids, especially acetone. These liquids absorb large volumes of acetylene, and under such conditions it is not explosive.

The chief use of the gas at the present time is in the cutting and welding of metals. It is likely that acetylene will be used extensively in the future as the starting material in the manufacture of a great variety of organic compounds.

Proof of Structure · The theory of structure of the hydrocarbons may seem arbitrary as it has been developed in this chapter. We may well ask, "What proof have we that the structures described thus far are actually the structures of the hydrocarbon molecules?" The proof of the structure of an organic molecule is usually based on (1) the *molecular formula*, derived from chemical analysis and molecular weight; and (2) *chemical properties*, the manner in which the molecule decomposes or reacts with other molecules; or (3) *synthesis*, the building up of the molecule out of simpler molecules or groups in such a way that we know defi-

nitely the manner in which the parts of the molecule are connected with one another.

Actual Proofs of the Structure of Some Hydrocarbons · In the following examples the Wurtz reaction (p. 516) is used to synthesize several hydrocarbons.

Example 1. The structure of ethane may be shown to be CH_3—CH_3 by the following steps: (1) The simplest ratio of atoms, as determined by analysis, is CH_3. However, the molecular weight is determined to be 30, and this leads to a molecular formula of C_2H_6. (2) The presence of two methyl groups is indicated by treating methyl bromide with sodium (Wurtz reaction). Ethane is formed, along with sodium bromide:

$$2\ CH_3Br + 2\ Na \longrightarrow C_2H_6 + 2\ NaBr$$

It is certain that the sodium takes up the bromine; and it is very plausible that the radicals, the residual methyl groups, each having a free valence bond, will pair up to form H_3C—CH_3, whatever the actual mechanism of joining may be.

Example 2. If ethyl bromide is treated with sodium, the product is butane (C_4H_{10}). According to the reasoning followed in the previous example, this compound would be formed by the union of two ethyl groups, and the product would be normal butane.

$$2\ CH_3—CH_2Br + 2\ Na \longrightarrow CH_3—CH_2—CH_2—CH_3 + 2\ NaBr$$

Since there are two known butanes, the one which is formed in this reaction would be assigned the structure of normal butane. The other should be isobutane.

Example 3. In order to check the conclusion in Example 2, an experiment may be carried out in which a mixture of methyl bromide (CH_3Br) and isopropyl bromide (CH_3—$CHBr$—CH_3) is treated with sodium. In this case there are three possible reactions, according to theory:

$$2\ CH_3Br + 2\ Na \longrightarrow CH_3—CH_3 + 2\ NaBr \qquad (1)$$

$$CH_3—CHBr—CH_3 + CH_3Br + 2\ Na \longrightarrow CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3 + 2\ NaBr \qquad (2)$$

$$2\ CH_3—CHBr—CH_3 + 2\ Na \longrightarrow \overset{1}{CH_3}—\underset{\displaystyle CH_3}{\overset{2}{\underset{|}{CH}}}—\underset{\displaystyle CH_3}{\overset{3}{\underset{|}{CH}}}—\overset{4}{CH_3} + 2\ NaBr \qquad (3)$$

The results of such an experiment do indeed show the formation of three products: ethane in equation (1); a butane (C_4H_{10}) in equation (2), different from that formed in Example 2 (and it must be *iso*butane); and a new compound (C_6H_{14}) in equation (3), which must have the structure shown, namely 2, 3-dimethylbutane.

There is, in addition, an inferential proof of the validity of the reasoning that we have been following. This proof depends on the agreement

between the predicted number of isomers and the number actually found in nature or prepared in the laboratory. Our theory, which we have developed briefly in preceding pages, tells us that there should be one and only one CH_4, one C_2H_6, and one C_3H_8; but that there should be two compounds whose formula is C_4H_{10}, three with the formula C_5H_{12}, five of C_6H_{14}, nine of C_7H_{16}, eighteen of C_8H_{18}, and so on. The actual facts are that only one CH_4, one C_2H_6, and one C_3H_8 have ever been found or prepared. There are two butanes and only two; three pentanes, five hexanes, nine heptanes, eighteen octanes, and so on. This exact agreement, without exception, of the theoretical number of isomers with the experimental number is one of the best proofs that we could have of the validity of the chemist's theory of the molecular structure of organic compounds.

QUESTIONS

1. Tell what is meant by each of the following (use examples where possible): (*a*) carbon chains; (*b*) carbon rings; (*c*) aliphatic compounds; (*d*) aromatic compounds; (*e*) hydrocarbon; (*f*) homologous series; (*g*) tetrahedral angle; (*h*) isomers; (*i*) normal isomer; (*j*) paraffin; (*k*) unsaturated compound; (*l*) cracking petroleum; (*m*) polymer.

2. Discuss the distinction between gasoline, kerosene, and lubricating oil in terms of boiling-point range and molecular composition.

3. (*a*) Write the structural formulas of the pentanes and the heptanes.

4. Write equations showing methods of preparation of (*a*) acetylene from lime, coke, and water; (*b*) ethylene from ethyl alcohol.

5. By means of the Wurtz synthesis show how *n*-hexane can be prepared.

6. (*a*) Write an equation for the reaction in each case when 1 mole of chlorine reacts with 1 mole of $C_{10}H_{20}$ and with 1 mole of $C_{10}H_{22}$. (*b*) How do you account for the different products?

7. Acetylene (C_2H_2) and benzene (C_6H_6) have the same percentage composition. What experimental data are necessary to determine the exact formulas?

8. Complete and balance the equations for the complete oxidation of the following hydrocarbons: (*a*) CH_4; (*b*) C_3H_8; (*c*) C_5H_{12}; (*d*) C_4H_8; (*e*) C_2H_2.

PROBLEMS

1. A certain gaseous hydrocarbon was found to contain 85.71 per cent carbon and 14.28 per cent hydrogen. (*a*) Calculate the simplest ratio of atoms in a molecule of this hydrocarbon. (*b*) If one liter weighs 2.5 g, calculate the molecular formula. (*c*) What is the name of the compound?

2. (*a*) What volume of oxygen under standard conditions is necessary to oxidize completely 100 g of each of the following: (1) CH_4; (2) C_6H_{14}; (3) C_9H_{20}? (*b*) What bearing does this have on the design of an automobile carburetor?

CHAPTER 29

SOME COMMON FAMILIES OF ORGANIC COMPOUNDS

Families of Carbon Compounds · The several hundred thousand known compounds of carbon can be classified in a few families; furthermore, all these families may be considered to be derivatives of the hydrocarbons. Examples of such families are alcohols, ethers, aldehydes, ketones, etc. We shall discuss several of them now. Each of these families has a set of characteristic properties, due to the presence in compounds of the family of a specific functional group (p. 510).

Alcohols, ROH

General · The alcohols are compounds which may be regarded as being derived from hydrocarbons by the substitution of one or more hydrogen atoms of the hydrocarbons by an equal number of hydroxyl groups. The simplest of these alcohols are those which contain one hydroxyl group in each molecule. These are called monohydric alcohols. A great many alcohols are known and, like the hydrocarbons, they may be arranged in homologous series. The relation between the first three members of the methane series of hydrocarbons and the corresponding monohydric alcohols is shown in the following table:

HYDROCARBONS AND THE MONOHYDRIC ALCOHOLS

HYDROCARBON	NAME	CORRESPONDING ALCOHOL	NAME
CH_4	Methane	CH_3OH	Methyl alcohol (wood)
C_2H_6	Ethane	C_2H_5OH	Ethyl alcohol (grain)
C_3H_8	Propane	C_3H_7OH	Propyl alcohol
C_nH_{2n+2} General formula		$C_nH_{2n+1}OH$ General formula	

Isomers of Alcohols · Alcohols with more than two carbon atoms can form isomers by having the OH group at more than one position on the carbon skeleton. For example, propyl alcohol can exist as

$CH_3—CH_2—CH_2OH$ and $CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$

normal propyl alcohol

isopropyl alcohol

Each of these is an isomer of the other, but the branched-chain one is usually called *iso*propyl and the other one *normal* propyl alcohol.

Properties of Alcohols · The monohydric alcohols of low molecular weight are liquids at room temperature. Like the members of other homologous series (p. 511), they show a regular gradation of properties with increasing carbon content (table below). For example, methyl alcohol (CH_3OH) is a liquid at ordinary temperatures; ethyl alcohol (C_2H_5OH) also is a liquid. Alcohols of higher molecular weight, such as cetyl alcohol ($C_{16}H_{33}OH$), on the other hand, are waxy solids at room temperature. The liquid members of the series are good solvents for many substances, such as greases and waxes, but are usually not good solvents for inorganic salts.

PROPERTIES OF THE SIMPLE MONOHYDRIC ALCOHOL

(The data are given for the normal isomer in each case)

ALCOHOL	FORMULA	BOILING POINT	MELTING POINT	DENSITY	SOLUBILITY IN 100 g OF WATER
Methyl	CH_3OH	65°	− 98°	0.793	Miscible
Ethyl	C_2H_5OH	78°	− 117°	0.789	Miscible
Propyl	C_3H_7OH	98°	− 127°	0.804	Miscible
Butyl	C_4H_9OH	118°	− 89°	0.810	9 g at 15°
Pentyl	$C_5H_{11}OH$	138°	− 78°	0.817	2.5 g
Hexyl	$C_6H_{13}OH$	156°	− 52°	0.820	Slight
Dodecyl	$C_{12}H_{25}OH$	255°	+ 23°	0.831	Insoluble

The lower members of the homologous series are soluble in water, but as the size of the hydrocarbon residue increases, the alcohols become less and less soluble in water.

While these compounds contain OH groups, they are not like hydroxides of the metals, nor like those of most of the nonmetals, since they are covalent compounds and therefore do not ionize. Hence they are neither bases nor acids.

Methyl Alcohol (Wood Alcohol) (CH_3OH) · Methyl alcohol, often called *methanol*, is formed when hardwoods, especially beech and birch, are heated in the absence of air; hence the name wood alcohol. Wood distillation long furnished us with our entire supply of methyl alcohol. At present, however, most of the methyl alcohol is prepared by heating a mixture of carbon monoxide and hydrogen under pressure and in contact with a suitable catalyst, such as the oxide of zinc or chromium:

$$CO + 2\,H_2 \longrightarrow CH_3OH$$

Methyl alcohol is a colorless liquid. It burns with an almost colorless flame. It is a good solvent for organic substances and is used in the manu-

facture of varnishes. Its chief use is in the manufacture of formaldehyde and of aniline dyes, and as a denaturant for grain alcohol. It is poisonous, and many deaths have resulted from its use as an intoxicant (p. 526).

Ethyl Alcohol (Ethanol, Grain Alcohol) ***(C_2H_5OH)*** · Ethyl alcohol, sometimes called *ethanol*, is a colorless liquid and has a characteristic odor different from that of methyl alcohol. It resembles methyl alcohol in its general properties. When ignited, it burns with a hot flame which does not deposit carbon. When taken into the system in small quantities it is intoxicating. The intoxicating properties of such liquors as beer, wine, and whisky are due to the alcohol present.

Preparation of Ethyl Alcohol · About 60 per cent of the ethyl alcohol is prepared from ethylene (p. 518); about 40 per cent is prepared by the process of *fermentation*. In this process a complex chemical compound, known as an *enzyme*, acts as a catalyst to change certain sugars into alcohol. Enzymes for fermentation are produced by simple plant forms, such as yeast, which in growing secrete the enzyme zymase. The reaction which occurs is

$$\underset{\text{sugar}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} 2\,C_2H_5OH + 2\,CO_2$$

Cane sugar, $C_{12}H_{22}O_{11}$, does not ferment directly, but the addition of yeast to its aqueous solution first changes the sucrose into simpler sugars of the formula $C_6H_{12}O_6$ (by the action of invertase, another catalyst formed in the growth of yeast). The sugars ferment through the catalytic action of zymase. The fermentation of the sugar in crude molasses is an important commercial source of alcohol. The fermentation of the sugar in grape juice produces wine.

Alcohol may be prepared also from the starch of grains by allowing the grains to sprout. The growing grain contains the enzyme diastase, which changes the starch into maltose; and then yeast is added to set up alcoholic fermentation.

$$\text{Starch} \xrightarrow[\text{(sprouting grains)}]{\text{diastase}} \text{maltose} \xrightarrow[\text{(growing yeast)}]{\text{maltase}} \text{alcohol} + \text{carbon dioxide}$$

This is the process which takes place in the preparation of beer and whisky.

The enzymes formed by the action of living organisms catalyze many chemical reactions such as fermentation, digestion, and decay, and play an important role in the metabolism of plants and animals. Enzymes are specialists in that each one appears to be capable of catalyzing a specific type of chemical reaction.

Chemical Changes in Breadmaking · An interesting application of alcoholic fermentation is found in the process for making bread from wheat flour. The average composition of wheat flour is as follows:

Water	11.9 per cent
Protein	13.3 per cent
Fats	1.5 per cent
Starch	72.7 per cent
Mineral matter	0.6 per cent

In making bread, flour is mixed with water, yeast, salt, and a little sugar, and the resulting dough is set aside in a warm place for a few hours. The yeast first causes the sugar to undergo alcoholic fermentation. The carbon dioxide formed escapes through the dough, making it light and porous. The yeast plant thrives best at about 30°; hence the necessity for keeping the dough in a warm place. When bread is baked, the heat expels the alcohol and also expands the bubbles of carbon dioxide caught in the dough, causing it to become more porous and making the bread light.

Absolute Alcohol · The water solution of alcohol obtained from the fermentation process may be concentrated by fractional distillation to a constant-boiling solution containing 96 per cent of alcohol. Further removal of water requires a dehydrating agent such as lime (CaO) followed by distillation. The resulting product is called absolute alcohol.

Production and Uses of Ethyl Alcohol · Normally more than 470,000,000 gal of alcohol (calculated as 100 per cent C_2H_5OH) is produced annually in the United States. Most of this is denatured by adding foul tasting or poisonous materials to make it unfit for beverage purposes without impairing its value for industrial use. Large quantities are used as antifreeze in automobile radiators in winter. Large quantities are also used in the manufacture of the various products made from cellulose and in the manufacture of lacquers, shellacs, varnishes, vinegar, toilet preparations, drugs, and various chemicals and dyes.

Chemical Reactions of Alcohols · The reactions of alcohols involve that portion of the alcohol molecule which contains the —OH group, since this is the most reactive section of an alcohol molecule.

1. **Reaction with sodium.** Metallic sodium acts on alcohols to replace the hydrogen atom attached to the oxygen atom:

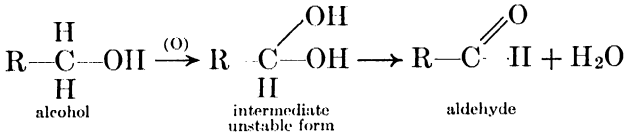
$$2\ CH_3CH_2OH + 2\ Na \longrightarrow 2\ CH_3CH_2ONa + H_2$$

2. **Esterification with organic acids.** Alcohols react with acids to form esters. Esters are derivatives of the acids in which the RO group of the alcohol has taken the place of the OH group of the acid. The structure of organic acids will be discussed later, but here we can show, by an equation, the reaction between ethyl alcohol and acetic acid:

$$\underset{\text{alcohol}}{C_2H_5OH} + \underset{\text{acid}}{CH_3CO{-}OH} \xrightarrow{H_2SO_4} \underset{\text{ester}}{CH_3COOC_2H_5} + \underset{\text{water}}{H_2O}$$

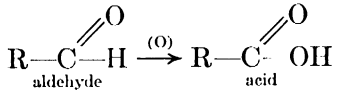
3. **Dehydration.** The removal of water from an alcohol can take place in either of two ways: by the formation of an unsaturated hydrocarbon by the removal of water from a single molecule (p. 517) or by the removal of water between two molecules, forming an ether (p. 532).

4. **Oxidation.** Alcohols can be oxidized completely to CO_2 and H_2O; they can also be oxidized in a stepwise manner to give several intermediate compounds; the reactions are carried out with such oxidizing agents as permanganic and chromic acids. These oxidizing agents react differently with different alcohols. On the mild oxidation of a *primary* alcohol (those with the CH_2OH group) a compound called an *aldehyde* is first formed. This will then oxidize to a carboxylic acid.

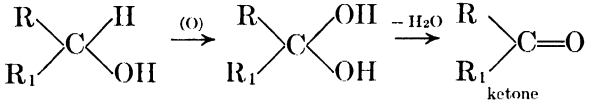


NOTE. As a rule when 2 or more OH groups are attached to the same carbon atom the molecule is unstable. It becomes stabilized by splitting off a molecule of water.

On further oxidation another hydroxyl group is formed, giving a carboxylic acid.



Secondary alcohols (those with the $>CHOH$ group) undergo only the first of these steps because there is only one hydrogen atom to be oxidized, forming a *ketone*.



Physiological Effects of Alcohols · Methyl alcohol has a specific effect on the optic nerve and produces blindness if taken internally or if the vapor is inhaled in large amounts. Ethyl alcohol seems to have a specific effect of such a sort that the higher levels of the central nervous system are cut off from the lower, and irrational drunkenness occurs. The higher alcohols become increasingly more toxic as the molecular weight increases; that is, propyl is more toxic than ethyl, butyl than propyl, etc. Fusel oil, which is a mixture of propyl, *n*-butyl, and several of the five-carbon-atom (amyl) alcohols, is present in small amounts in most raw spirits and is thought to be very toxic.

Proof of the Structure of Methyl Alcohol · The structural formula of a compound may be deduced in two logical steps, as has already been shown (p. 520): (1) after the molecular formula has been determined, (2) the chemical reactions that a compound undergoes will usually give a clue as to how the atoms are arranged within the molecule; and often synthesis of the compound gives confirming evidence of its structure.

1. In the case of methanol, chemical analysis and molecular-weight determinations show the molecular formula to be CH_4O.

2*a*. In the reactions which methanol undergoes, one of the four hydrogen atoms behaves differently from the others. For example, metallic sodium reacts with methanol to liberate one of the hydrogen atoms.

$$2\ CH_4O + 2\ Na \longrightarrow 2\ CH_3ONa + H_2$$

This reaction is strongly reminiscent of the action of sodium on water,

$$2\ H_2O + 2\ Na \longrightarrow 2\ HONa + H_2$$
$$(NaOH)$$

b. By reaction with phosphorus trichloride, PCl_3, the oxygen atom and a hydrogen atom are removed, just as in the similar reaction with water:

$$3\ CH_4O + PCl_3 \longrightarrow 3\ CH_3Cl + P(OH)_3$$
$$3\ H_2O + PCl_3 \longrightarrow 3\ HCl + P(OH)_3$$

c. We know that the atoms in water are connected as H—O—H, and the similarity in reactions leads us to conclude that in methanol, too, one of the hydrogen atoms is connected to the oxygen atom.

If this is true, then the tetravalency of carbon permits only the structure $CH_3—OH$.

Aldehydes, $R—\overset{\overset{O}{\|}}{C}—H$, and Ketones, $R_2C{=}O$

General · These two classes of compounds may be formed by the mild oxidation of alcohols, as described above. The symbol R in their formulas represents any *alkyl* group, such as CH_3 or C_2H_5. The functional group, $—\overset{\overset{O}{\|}}{C}—H$ characterizes the aldehydes, and $\rangle C{=}O$ the ketones. In these compounds, as in most organic compounds, the hydrocarbon residues are relatively inert, and the chemical properties are primarily those of the functional groups. For example, the two compounds CH_3CHO and

CH_3CH_2CHO will act alike chemically because chemical reactivity is for the most part confined to the reactions of the functional group —CHO.

Chemical Reactions of Aldehydes and Ketones · Both aldehydes and ketones contain the carbonyl group $\rangle C{=}O$, and most of their reactions are those which are characteristic of this group. In the aldehydes one of the valences of the C atom is connected to hydrogen; in consequence, the carbonyl group of an aldehyde is in general more reactive than that of a ketone of about the same molecular weight.

Some common reactions of aldehydes and ketones are as follows:

1. **Oxidation.** Aldehydes are readily oxidized to the corresponding acids and are, in consequence, good reducing agents:

$$R{-}C(=O){-}H \xrightarrow{(O)} R{-}C(=O){-}OH$$

Ketones do not oxidize except with strong oxidizing agents, and then only with breaking of the hydrocarbon chain to form compounds of lower molecular weight. This resistance to oxidation serves to distinguish ketones from aldehydes.

2. **Reduction.** Aldehydes can be reduced to primary alcohols; ketones form secondary alcohols (see page 526).

3. **Polymerization.** Molecules containing aldehyde groups have a tendency to combine with one another (polymerize), with the formation of compounds of high molecular weight. If, for example, we think of the double bond of an aldehyde as opening up, thus:

$$\begin{matrix} R \\ C{=}O \\ H \end{matrix} \longrightarrow \begin{matrix} R \\ -C- \\ H \end{matrix} O-$$

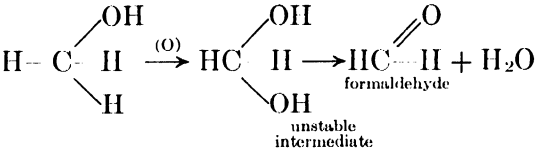
we can picture chain-formation taking place as follows:

$$\begin{matrix} R \\ C \\ II \end{matrix} O- + \begin{matrix} R \\ -C- \\ H \end{matrix} O- + \begin{matrix} R \\ -C- \\ H \end{matrix} O- \longrightarrow \begin{matrix} R \\ -C \\ H \end{matrix} O \begin{matrix} R \\ C- \\ H \end{matrix} O \begin{matrix} R \\ -C- \\ H \end{matrix} O-$$

Such a reaction can continue until the terminal valences are satisfied by some side reaction or by ring formation, so that a variety of products, of different molecular sizes, are possible.

Some Simple Aldehydes and Ketones · Aldehydes are commonly named from the acids which they yield when they are oxidized. Thus $CH_3{-}CHO$ is called acetaldehyde, from acetic acid ($CH_3{-}COOH$).

The simplest aldehyde is *formaldehyde*, $H{-}C(=O){-}H$. It is formed by the partial oxidation of wood alcohol (CH_3OH):



It can frequently be detected in the air around a gas stove which is burning inefficiently with consequent incomplete combustion of the gas, the chief component of which is methane (CH_4). Formaldehyde (HCHO) produces a sharp, irritating sensation when its vapors come in contact with the mucous membrane; it has a sickening, suffocating odor. It is very soluble in water, and a 40 per cent aqueous solution is sold on the market as formalin. Formalin is used for preserving biological specimens, as an embalming fluid, as a fumigating agent (both as an insecticide and as a disinfectant), and as a reagent in making organic compounds.

Acetaldehyde is formed by the mild oxidation of ethanol, and is easily oxidized to acetic acid (CH_3COOH). Its main use is in the synthesis of organic compounds. The chlorinated derivative of acetaldehyde, chloral (CCl_3CHO), is used extensively in medicine as a soporific (sleep-producer). It is sold as chloral hydrate, having the formula $CCl_3CH(OH)_2$, one of the few cases where a molecule with two hydroxyl groups on the same carbon atom is stable.

The common ketone is *acetone* ($CH_3—CO—CH_3$). Ketones may be named from the groups attached to the carbonyl group; thus $CH_3—CO—CH_3$ is dimethyl ketone; $C_2H_5—CO—CH_3$ is methyl ethyl ketone.

The ketones of lower molecular weight are volatile liquids with pleasant odors. Acetone is an excellent solvent for many organic compounds and is much used in lacquers.

Carboxylic Acids, $R—\overset{\overset{O}{\|}}{C}—OH$

An important class of organic compounds is formed by the mild oxidation of aldehydes, producing the —COOH group. This is the functional group of an organic acid; it is called the *carboxyl* group and has the structural formula $—\overset{\overset{O}{\|}}{C}—OH$. This structural formula illustrates another rule of organic chemistry, namely, that any hydrogen atom attached through an oxygen atom to a carbon atom which has a double bond will

be acidic. The reason for this is deep-seated in the electronic nature of the double bond.

The oxidation of aldehydes to acids has been shown on page 528.

The carboxyl group (—COOH) undergoes two interesting types of reactions: (1) it can ionize in water, forming H^+ ions, and hence serve as an acid; and (2) its OH group can be replaced by other atoms or groups.

Properties of Acids · 1. **Acid character.** The organic acids as a class differ from most organic compounds in that they ionize. Those which are soluble in water are weakly acidic, as indicated by the equilibrium

$$\underset{\text{acetic acid}}{CH_3COOH} \rightleftarrows \underset{\text{acetate ion}}{CH_3COO^-} + \underset{\text{hydrogen ion}}{H^+}$$

The only hydrogen that ionizes in acetic acid or any organic acid is the one contained in the carboxyl group of the acid. Organic acids form salts with strong bases:

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

2. **Esterification.** Acids readily form esters with alcohols (p. 525):

$$R\text{—}COOH + R\text{—}OH \longrightarrow R\text{—}COOR + H_2O$$

Acetic Acid · The first four of the acids related to the methane series of hydrocarbons are

$HCOOH$	formic acid
CH_3COOH	acetic acid
CH_3CH_2COOH	propionic acid
$CH_2CH_2CH_2COOH$	butyric acid

The most important of these, acetic acid, is the acid which gives the sour taste to vinegar. It is prepared commercially by the distillation of wood, as well as by the oxidation of dilute alcohol. It is a colorless liquid and has a strong, pungent odor. When anhydrous, it crystallizes as a colorless solid which melts at 16.6° and closely resembles ice in appearance; hence the name *glacial acetic acid.* Many of the salts of acetic acid are well-known compounds; for example, lead acetate $(CH_3COO)_2Pb \cdot 3\,H_2O$, which is a white salt called *sugar of lead.* Paris green is a mixed salt of copper acetate and copper arsenite $Cu(C_2H_3O_2)_2 \cdot 3\,Cu(AsO_2)_2$.

Vinegar · When cider is exposed to the air, it is gradually transformed into vinegar. Two changes are involved in the process: (1) the sugar in the cider undergoes alcoholic fermentation, with the formation of *hard cider,* which contains from 4 to 8 per cent of alcohol; (2) the alcohol is then oxidized to acetic

acid by the oxygen of the air. This oxidation is brought about by certain bacteria, and is called acetic fermentation. It may be represented as follows:

$$\underset{\text{alcohol}}{CH_3CH_2OH} + O_2 \longrightarrow \underset{\text{acetic acid}}{CH_3COOH} + H_2O$$

Manufacture of Vinegar · The rate of acetic fermentation may be greatly increased by providing intimate contact between the alcohol solution and the oxygen of the air. This may best be accomplished by loosely filling a large cask (*generator*) with beech shavings, spraying vinegar into the top of the cask to introduce the bacteria, and then similarly spraying a dilute solution of alcohol (hard cider, in the case of cider vinegar), while admitting air at the bottom. The resulting vinegar is drawn off at the bottom of the cask.

Instead of starting with cider, one may use almost any substance which contains starch or sugar; for these compounds change into alcohol, as explained in the paragraphs on the manufacture of alcohol. In this way *malt vinegar* is prepared from starch and *sugar vinegar* from sugar residues. The cheapest vinegar is made from pure dilute alcohol and is known as *distilled vinegar*. It is colorless and leaves almost no residue upon evaporation.

A Federal law requires that all vinegar shall contain not less than 4 per cent acetic acid. Vinegar prepared from fruits and grains contains certain solids derived from the source materials. By studying the character of these solids the chemist is able to determine the source of the vinegar.

Esters, $RC(=O)—OR$

Organic acids will react with alcohols to form esters (pp. 525, 530):

$$\underset{\text{acid}}{CH_3C(=O)—OH} + \underset{\text{alcohol}}{C_2H_5OH} \longrightarrow \underset{\text{ester}}{CH_3C(=O)—OC_2H_5} + \underset{\text{water}}{H_2O}$$

This reaction, called esterification, is best carried out in the presence of some substance such as sulfuric acid, which serves as a catalyst and also removes the water which is formed; otherwise an equilibrium results in which the ester formed reacts with the water to form the alcohol and the acid again.

It is of further interest that the reaction results in the loss of the acid hydroxyl group and the hydrogen atom of the alcohol rather than the hydrogen atom of the acid and the hydroxyl group of the alcohol. This mechanism has been proved with oxygen isotopes as tracer elements.

Saponification · When an ester is treated with a strong base, such as sodium or potassium hydroxide, it reacts, slowly, giving an alcohol and a salt of the organic acid:

$$RC(=O)—OR_1 + NaOH \longrightarrow RC(=O)—ONa + R_1OH$$

Ethyl acetate, for example, reacts with sodium hydroxide as follows:

$$CH_3C(=O)OCH_2CH_3 + NaOH \longrightarrow CH_3COONa + CH_3CH_2OH$$

This is the one most common chemical reaction which esters undergo; it is called saponification. It is the important reaction in the manufacture of soap, and derives its name from this fact (p. 539).

Esters are named from the alkyl group and the acid ion:

$CH_3COOC_2H_5$ is ethyl acetate.
$CH_3COOC_3H_7$ is propyl acetate.

The esters are colorless liquids or solids with pleasant, fruity odors. Many of the natural oils contain esters, and the pleasant odors of fruits and flowers are largely due to their presence. Amyl acetate smells like bananas and is called banana oil.

	ESTER	ODOR
ODORS OF SOME COMMON ESTERS	Isoamyl acetate	banana oil
	Amyl butyrate	apricot, cider
	Isoamyl isovalerate	apple
	Ethyl butyrate	apricot, peach
	Ethyl heptoate	synthetic cognac
	Ethyl nonylate	fancy bouquets
	Ethyl laurate	tuberose
	Ethyl undecylenate	powerful violet odor
	Methyl butyrate	pineapple
	Methyl myristate	powerful orris odor
	Octyl acetate	orange

The esters are good solvents for many organic materials and are much used as solvents for lacquers, such as fingernail polish. Also, they have limited use in the making of artificial flavors.

Ethers, R—O—R

The elimination of water from two molecules of an alcohol yields an ether; for example, ethyl alcohol yields diethyl ether:

$$\left.\begin{matrix} CH_3CH_2—O\!\!\!\diagup H \\ CH_3CH_2—O\!\!\!\diagup H \end{matrix}\right\} \longrightarrow CH_3CH_2—O—CH_2CH_3 + H_2O$$

This reaction is carried out most conveniently in the presence of sulfuric acid, which serves as the dehydrating agent.

If other alcohols are used instead of ethyl alcohol, a variety of ethers may be formed. The two alcohols involved may be the same or different The ether is named by designating the alkyl groups:

CH_3OCH_3 is dimethyl ether (methyl ether).
$CH_3OC_2H_5$ is methyl ethyl ether.
$C_2H_5OC_2H_5$ is diethyl ether (ethyl ether).
$C_2H_5OC_3H_7$ is ethyl propyl ether.

Ethers are like the hydrocarbons in that they are not reactive toward most of the common reagents; those of lower molecular weight are inflammable. They have a characteristic sweet odor. They are good solvents for many organic substances, including resins and plastics.

Ethyl ether is the one most commonly used. It is a colorless liquid which boils at 35° and is used as an anesthetic in surgical operations. Isopropyl ether has a much higher boiling point, and hence is much safer for use as a solvent because the danger of fire is less.

The Williamson Synthesis as Proof of the Structure of Ethers · After the molecular formula of an ether has been found, the structure may be determined by the Williamson reaction. This consists in treating a sodium or potassium alcoholate with an alkyl halide:

$$CH_3CH_2ONa + CH_3CH_2Br \longrightarrow CH_3CH_2OCH_2CH_3 + NaBr$$

Williamson prepared methyl ethyl ether both by treating sodium ethylate with methyl bromide and by treating sodium methylate with ethyl bromide:

$$CH_3CH_2ONa + CH_3Br \longrightarrow CH_3CH_2OCH_2 + NaBr$$
$$CH_3ONa + CH_3CH_2Br \longrightarrow CH_3OCH_2CH_3 + NaBr$$

Since sodium bromide is definitely formed and since nothing other than the ether is formed in each case, we naturally conclude that the ethers then contain two alkyl groups attached through an oxygen atom.

Nitrogen-Containing Compounds

There are many organic compounds which contain nitrogen; among these are the nitriles, R—CN, the amines, R—NH_2, and the amides, R—C(=O)—NH_2. For many purposes these may be considered to be derivatives of ammonia, in the same way that oxygen compounds might be considered as derivatives of water Allowance must be made for the fact

that nitrogen is trivalent, whereas oxygen is only bivalent. A suggestive analogy is shown in the following scheme:

OXYGEN COMPOUND		NITROGEN COMPOUND	
water	HOH	ammonia	$H \cdot NH_2$
alcohol	ROH	primary amine	$R \cdot NH_2$
ether	ROR	secondary amine	R_2NH
		tertiary amine	R_3N
ketone	$R_2C{=}O$	ketimine	$R_2C{=}NH$
aldehyde	$RC(=O)H$	aldehyde imine	$RCH{=}NH$
acid	$RC(=O)OH$	amide	$RC(=O)NH_2$
ester	$RC(=O)OR$	substituted amides	$RC(=O)NHR$, $RC(=O)NR_2$

The properties of the nitrogen compounds differ from those of the oxygen compounds chiefly because nitrogen confers a more basic character upon its compounds, as may be seen by comparing ammonia and water. Like ammonia, the amines are basic and form salts:

$$R{-}NH_2 + HCl \longrightarrow R{-}NH_3^+ + Cl^-$$

This is even more true of the tertiary amines:

$$R_3N + HCl \longrightarrow R_3NH^+ + Cl^-$$

The amides are much less acid than the corresponding oxygen compounds, showing almost no tendency to give off a hydrogen ion.

Sulfur, as well as nitrogen, may be present in organic compounds, often playing the role of oxygen in such compounds. For example, the compound thioacetamide, $CH_3{-}C(=S){-}NH_2$, is an analogue both of acetic acid, $CH_3{-}C(=O){-}OH$, and of acetamide, $CH_3{-}C(=O){-}NH_2$. Thioacetamide is used in qualitative analysis to produce hydrogen sulfide by hydrolysis:

$$CH_3{-}C(=S){-}NH_2 + 2\,H_2O \longrightarrow CH_3{-}C(=O){-}O^-, NH_4^+ + H_2S$$

QUESTIONS

1. Write structural formulas for all the alcohols whose general formula is C_4H_9OH.

2. Give the formulas and names of the products formed by the action of mild oxidizing agents on the above alcohols.

3. Define (*a*) *saponification*; (*b*) *esterification*. What are (*c*) absolute alcohol; (*d*) denatured alcohol; (*e*) a monohydric alcohol; (*f*) a primary alcohol; (*g*) an ester; (*h*) an ether?

4. Starting with methane show by equations how formaldehyde would be formed as a result of inefficient combustion in a gas stove.

5. Starting with ethyl alcohol (C_2H_5OH) show how the following can be made: (*a*) ethylene; (*b*) ethyl ether; (*c*) acetaldehyde; (*d*) ethyl acetate.

6. Show how the following reaction can be effected:

$$CH_3—CHOH—CH_3 \rightarrow CH_3—CO—CH_3$$

7. Methanol differs from all the other alcohols in that it has three hydrogen atoms attached to the same carbon atom as the hydroxyl group. Write equations to show all the products which can be formed by the stepwise oxidation of methanol.

8. Write equations for (*a*) the reaction which takes place between butyric acid and potassium hydroxide; (*b*) the saponification of ethyl propionate; (*c*) the action of metallic potassium on methyl alcohol.

9. Give the structure of the characteristic, or functional, group of (*a*) primary alcohols; (*b*) aldehydes; (*c*) ketones; (*d*) acids; (*e*) esters; (*f*) ethers.

10. Give a laboratory method and an industrial method for the preparation of (*a*) methyl alcohol; (*b*) ethyl alcohol; (*c*) acetone; (*d*) ethyl ether; (*e*) formaldehyde.

11. Write the structural formulas of (*a*) methyl formate; (*b*) ethyl acetate; (*c*) isopropyl acetate; (*d*) ethyl propionate.

12. Write structural formulas for each of the following: (*a*) ethylamine; (*b*) dimethyl amine; (*c*) ethyldimethylamine. Which of these is a primary amine? Which is a secondary amine? tertiary amine?

13. Write an equation showing the action (*a*) of ammonia with hydrogen chloride; (*b*) of each of the amines named in question 12 with hydrogen chloride.

14. Solutions of amines in water are basic. By analogy with ammonia show why this is so.

15. Ethyl acetate reacts with ammonia to form acetamide. What is the other product? Write an equation for the reaction.

16. There is a compound CH_3CH_2SH called ethyl mercaptan. In your opinion, would it be acid, basic, or neutral? Use the analogy between H_2O and H_2S in making up your mind.

CHAPTER 30

FATS; CARBOHYDRATES; PROTEINS

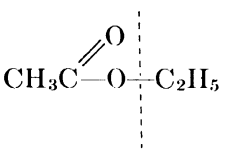
The organic compounds that we have discussed in the last chapter—alcohols, aldehydes, acids, ethers, etc.—are made up of rather simple molecules in that they have only one functional group. Most of their reactions are limited to those of their particular characteristic group. But there are many other kinds of organic compounds, and in this chapter we shall be interested in studying (1) fats, (2) carbohydrates, and (3) proteins, all three of which are among the principal constituents of food. Can these compounds be considered to be alcohols, or aldehydes, or ethers, or acids?

In this chapter we shall study these three classes of compounds found in foods. We shall examine the structures of their molecules to find what characteristic groups are present. In this manner we may be able to predict some of the properties we could expect these compounds to have. This will help to explain what happens to the molecules of food as they undergo some of the chemical reactions in digestion. This chapter will serve as an example of how the chemist studies the structure and composition of complex organic molecules.

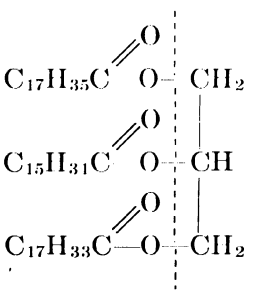
Fats

Fats are found in such things as butter, lard, tallow, and animal and vegetable oils. They are an important class of foods. In order to understand the chemical nature of a fat let us compare the formulas of the molecules of several fats with the formula of a simple ester.

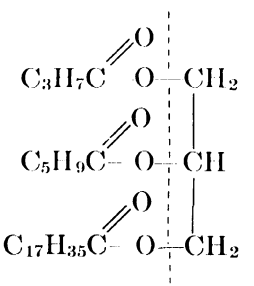
An ester molecule



Fat molecules



found in lard



found in butter

As we compare these formulas we find that they are similar in that they all contain an $RC(=O)-O-$ group which is attached to a hydrocarbon group. Thus a fat is an ester.

Now let us compare the products formed when an ester and a fat are saponified in alkali:

$$\underset{\text{ester}}{CH_3C(=O)-O-C_2H_5} + \underset{\text{alkali}}{NaOH} \longrightarrow \underset{\text{sodium salt}}{CH_3C(=O)-O^-, Na^+} + \underset{\text{alcohol}}{C_2H_5OH}$$

$$\begin{array}{l} C_{17}H_{35}C(=O)-O-CH_2 \\ C_{15}H_{31}C(=O)-O-CH \\ C_{17}H_{33}C(=O)-O-CH_2 \\ \text{fat} \end{array} + \begin{array}{l} NaOH \\ NaOH \\ NaOH \\ \text{alkali} \end{array} \longrightarrow \begin{array}{l} C_{17}H_{35}C(=O)-O^-, Na^+ \\ C_{15}H_{31}C(=O)-O^-, Na^+ \\ C_{17}H_{33}C(=O)-O^-, Na^+ \\ \text{sodium salt (called soap)} \end{array} + \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \\ \text{glycerol (a trihydric alcohol)} \end{array}$$

The reactions are similar; in both cases a salt and an alcohol are formed. Hence from comparison of (1) the functional groups and (2) the types of reaction we conclude that a fat is an ester; but it is an ester of glycerol, a *trihydric* alcohol (one with three hydroxyl groups). A fat is a glyceryl ester, usually of long-chain carboxylic acids.

Glyceryl Esters · Organic acids will react with glycerol to form an ester, in much the same way that other alcohols, such as ethyl alcohol, are esterified. If stearic acid ($C_{17}H_{35}COOH$) is used, the product is then glyceryl tristearate (tristearin); it is the main constituent of lard:

$$\begin{array}{l} C_{17}H_{35}COOCH_2 \\ | \\ C_{17}H_{35}COOCH \\ | \\ C_{17}H_{35}COOCH_2 \end{array}$$

tristearin

If oleic acid ($C_{17}H_{33}COOH$) is esterified with glycerol, the corresponding trioleate (olein) is formed, while with palmitic acid ($C_{15}H_{31}COOH$) the tripalmitate (palmitin) is formed. These esters also are found in lard and other fats.

There may be mixed esters also. For example, if a mixture of palmitic, oleic, and stearic acids were used, we should obtain the compound given on page 536.

The tristearate and the tripalmitate are solids of relatively high melting points. The trioleate is a liquid. Mixed esters have melting points which vary with the amount of oleic acid in the fat or oil. If the amount of combined oleic acid is high, the glyceryl ester is a liquid fat.

Butter; Oleomargarine · Butterfat, like other fats, consists principally of glyceryl esters of oleic, palmitic, and stearic acids, but its characteristic flavor is due to the presence of small quantities of other acids, such as butyric acid, combined with the glycerol. Oleomargarine differs from butter mainly because it contains a smaller percentage of the characteristic butter esters. It is made from vegetable oils, such as those obtained from coconuts, soybeans, and cottonseed, and from fats obtained from cattle and hogs. These oils and fats are sometimes churned with milk or mixed with a small quantity of butter in order to impart a butter flavor to the oleomargarine.

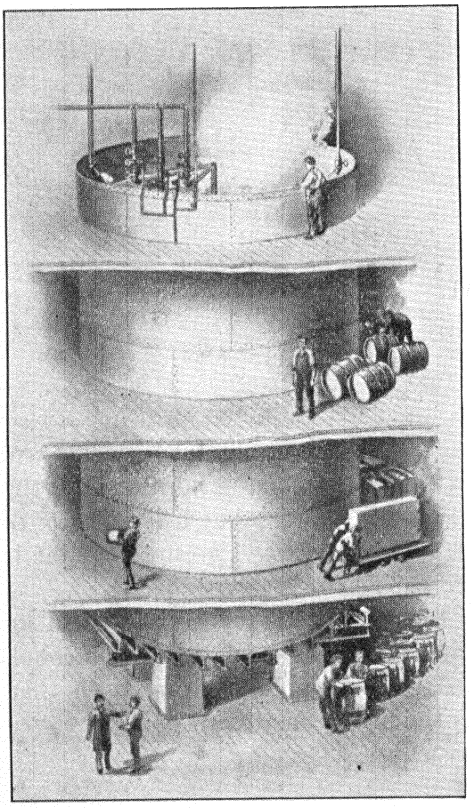


Fig. 30-1. The Manufacture of Soap · The melted fat or oil, mixed with a solution of sodium hydroxide, is heated in large iron kettles

Hydrogenation of Oils; Lard Substitutes · Oleic acid differs from stearic acid only by the presence of a double bond (p. 517); and the vegetable oils differ from the solid fats primarily because of the relatively high percentage of the esters of oleic acid in the former. It is undoubtedly true, therefore, that the low melting point which makes oleic acid and its esters liquid at ordinary temperatures must be the result of the presence of the double bond; hence all that is necessary to change a vegetable oil into a solid fat is to "hydrogenate" it by adding two hydrogen atoms at the double bond. This "hydrogenation" is brought about by heating the oil with hydrogen under pressure in the presence of a nickel catalyst. Many hydrogenated vegetable oils are now on the market as lard substitutes. Often such prepared fats are "fortified" with vitamins

to improve their nutritional value. Fats that are taken into the digestive system are converted to glycerol and the salts of the acids (p. 537).

Saponification; Manufacture of Soap · When a fat or oil is heated with sodium or potassium hydroxide, saponification takes place; that is, glycerol and the salt of the acid are formed. This is the reaction that occurs in the manufacture of soap from a fat.

The reactions in soapmaking are carried out in large kettles heated by steam (Fig. 30-1). Over 500,000 lb of soap is often made in a single heating.

Properties of Soap · When soap is added to water, it apparently dissolves. Experiment shows, however, that some of the soap is present in the form of a colloidal dispersion. Some hydrolysis takes place, so that the liquid is basic in character. The calcium and magnesium salts of oleic, palmitic, and stearic acids are insoluble in water, so that they are precipitated when a calcium or magnesium compound is added to an aqueous solution of soap:

$$\underset{\text{sodium stearate}}{2\ C_{17}H_{35}COONa} + CaCl_2 \longrightarrow 2\ NaCl + \underset{\text{calcium stearate}}{(C_{17}H_{35}COO)_2Ca}\downarrow$$

It is for this reason that soaps do not lather with hard waters but form a curdy precipitate, since such waters always contain salts of calcium and magnesium in solution.

The cleansing action of soap is explained in the same way as is the stabilization of emulsions (Fig. 26-14, p. 477). When soapy water is rubbed on the skin, any fatty or greasy substances present are emulsified by the soap and then washed away.

Other Detergents · Other and newer detergents have certain distinct advantages over soap. For example, the long-chain sulfates, $CH_3(CH_2)_n{-}O{-}SO_2{-}ONa$, where n is 10 or greater, act like soap in hard as well as in soft water, and are effective in acid waters, which would precipitate the fatty acids from ordinary soaps.

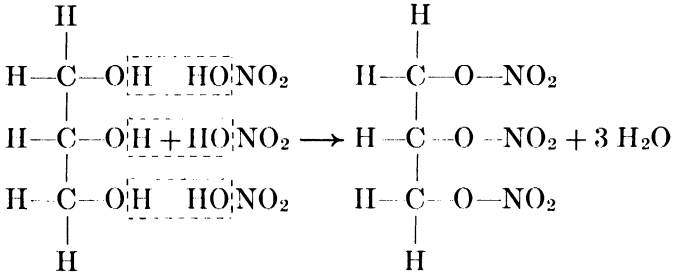
Glycerol and Other Polyhydric Alcohols · Glycerol, $C_3H_5(OH)_3$, is an example of many alcohols that have more than one OH group in each molecule (polyhydric alcohols). The hydroxyl groups in polyhydric alcohols are always attached to different carbon atoms; this must be true, since two hydroxyl groups on the *same* carbon atom tend to lose the elements of water (p. 526).

The most important and simplest trihydric alcohol is glycerol (commonly called glycerin), p. 537. It is a very viscous liquid which is soluble in water and has a sweet taste. It boils at 290°.

Glycerol combines with organic acids, usually palmitic, oleic, and stearic acids, to form esters which are found in ordinary fats. It is formed

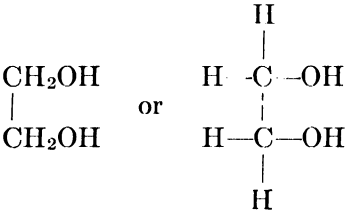
in the process of soapmaking, and is a by-product of the soap industry. It can be made also from propylene ($CH_2{=}CH{-}CH_3$).

Glycerol contains two primary alcohol groups and one secondary. It possesses the properties associated with such groups. The most important of these is ester formation. Glycerol may be esterified with either organic or inorganic acids. If it is treated with nitric acid in the presence of sulfuric acid, glyceryl trinitrate (nitroglycerin) is formed:

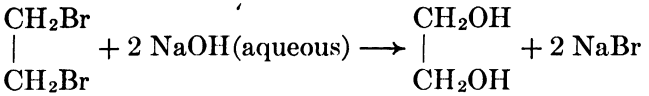


Glyceryl trinitrate is an oily liquid of slightly yellowish color; it is very explosive. It explodes by pressure or shock, by detonation, or by being heated to 250°.

Dihydric Alcohols · The simplest *dihydric* alcohol is ethylene glycol, which may be represented structurally thus:



Ethylene glycol is a sirupy liquid which is very soluble in water. It boils at 198°. It is sold under the name Prestone as an antifreeze for automobiles. It can be made by the reaction shown in the following equation:



Ethylene glycol undergoes the usual reactions of primary alcohols.

Carbohydrates

General · Carbohydrates are probably the most abundant of all the organic compounds in the plant kingdom. They include such commonly known compounds as sugars, starches, and cellulose. Some of them are

formed in nature, by photosynthesis, from carbon dioxide and water (p. 108). Carbohydrates contain carbon, hydrogen, and oxygen, and in most of the common members of the group the hydrogen and oxygen are present in the proportion in which they combine to form water. The carbohydrates are not only the probable original sources of all our body and fuel energy, but also the starting materials out of which plants and animals make, synthetically, practically all the many organic compounds found in nature. The most important carbohydrates are the following:

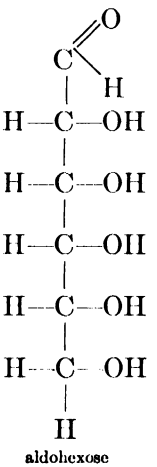
IMPORTANT CARBOHYDRATES

Sucrose (ordinary sugar)	$C_{12}H_{22}O_{11}$	Fructose (fruit sugar)	$C_6H_{12}O_6$
Lactose (milk sugar)	$C_{12}H_{22}O_{11} \cdot H_2O$	Starch	$(C_6H_{10}O_5)_x$
Maltose (malt sugar)	$C_{12}H_{22}O_{11} \cdot H_2O$	Cellulose	$(C_6H_{10}O_5)_x$
Glucose (grape sugar)	$C_6H_{12}O_6$	Xylose (a pentose)	$C_5H_{10}O_5$

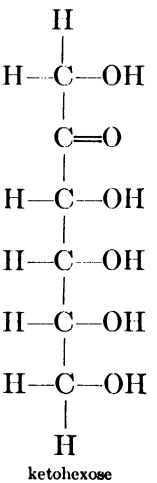
The more complex carbohydrates are condensation products of two or more molecules of the simple carbohydrates (called saccharide units). The molecular formulas of cellulose and starch are multiples of the simple formula $C_6H_{10}O_5$; accordingly, they are often written $(C_6H_{10}O_5)_x$, in which x is somewhere between 26 and 30 for starch and between 100 and 3000 for cellulose.

Carbohydrates are classified as monosaccharides, disaccharides, or polysaccharides, depending upon the number of saccharide units in each molecule of the carbohydrate. The names of these saccharide units have the ending *-ose*. Most of the naturally occurring monosaccharides contain five or six carbon atoms; those with five carbon atoms are called pentoses, and those with six are called hexoses.

Simple Sugars (Monosaccharides) · The simple sugars of six carbon atoms have general formulas as follows:



aldohexose



ketohexose

These formulas indicate that simple sugars are made of polyfunctional molecules. They are really polyhydric alcohols that contain either an aldehyde or a ketone group. Hence they can be expected to show the properties and to undergo the reactions of alcohols (both primary and secondary) and of either aldehydes or ketones. Indeed, their structures have been identified by observing that these simple sugars undergo just such reactions.

A Common Monosaccharide: Glucose (Grape Sugar, Dextrose) ***($C_6H_{12}O_6$)*** · Glucose is present in many fruits. It is an aldose, and is usually associated with fructose, a ketose. Glucose is often called grape sugar because of its presence in grape juice. Commercially it is prepared by heating starch with water to which hydrochloric acid (a hydrolysis catalyst) has been added:

$$(C_6H_{10}O_5)_x + xH_2O \longrightarrow xC_6H_{12}O_6$$

When the change is almost complete, enough sodium carbonate is added to neutralize the hydrochloric acid, and the solution is then concentrated to a sirup by evaporation. This sirup, which may contain other products of the decomposition of starch, such as maltose and dextrin, is called corn sirup. It is prepared in enormous quantities for use as a constituent of candies, jellies, jams, sirups, and other sweets.

Pure glucose is a white crystalline solid which resembles cane sugar in its properties, but is only about half as sweet. It is an inexpensive and healthful food. A small percentage (about 0.1 per cent) is present in the blood of persons in good health, and a much larger percentage in the blood of persons afflicted with diabetes. Glucose will ferment, in the presence of certain enzymes, especially the zymase of yeast, to form alcohol:

$$C_6H_{12}O_6 \xrightarrow{\text{enzyme}} 2\ C_2H_5OH + 2\ CO_2$$

Fructose (Fruit Sugar, Levulose) ***($C_6H_{12}O_6$)*** · Fructose is a white solid which occurs, along with glucose, in fruits and honey. It is even sweeter than sucrose, and is one of the ketohexose isomers.

A Common Disaccharide: Sucrose (Sugar) ***($C_{12}H_{22}O_{11}$)*** · Sucrose, or ordinary sugar, is called a disaccharide because it contains two monosaccharide units: $C_{12}H_{22}O_{11} + H_2O \longrightarrow 2\ C_6H_{12}O_6$. Sucrose, known from very ancient times, occurs in many plants, especially in the sugar cane and sugar beet; and these two plants furnish practically all the world's supply. Sugar cane grows only in warm climates; Cuba and the Hawaiian Islands are the greatest producers. The sugar beet thrives in the cooler climates that prevail in Colorado and Nebraska and in Germany. The terms *cane* and *beet*, when applied to sugar, simply indicate

the source of the product. From either source it is the same compound, namely, sucrose. In 1953 the world production of sucrose was approximately 43,625,000 tons, or 33 pounds of raw sugar per person. The consumption in the United States in the same year was about 8.5 million tons, or about 95 pounds of refined sugar per capita.

When heated to 186°, sucrose melts; if the temperature is increased to about 215°, a partial decomposition takes place, and a brown substance, known as caramel, is formed. This is used extensively as a coloring matter and in making confectionery.

The Separation and Refining of Sugar · Sugar cane contains from 12 to 15 per cent of sucrose, and the sugar beet from 15 to 20 per cent. The juice extracted from these plants contains the sugar in solution, along with many impurities. These impurities are removed, and the solution is then evaporated until the sugar crystallizes.

Ordinary molasses is the solution which remains after a part of the sugar has been crystallized from the purified juice of the sugar cane. Brown sugar is partially purified cane sugar. The sweetness of maple sugar is due to sucrose; the distinctive flavor is imparted by other substances present in the maple sap. The annual consumption of sucrose in the United States amounts to about 100 lb for each inhabitant.

Lactose (Milk Sugar) ($C_{12}H_{22}O_{11} \cdot H_2O$) · The disaccharide lactose occurs in the milk of all mammals The average composition of cow's milk is as follows:

	PER CENT
Water	87.0
Casein (nitrogenous matter)	3.3
Butterfat	4.0
Lactose	5.0
Mineral matter	0.7

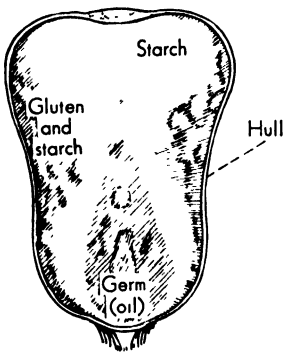
When rennin (a substance obtained from a calf's stomach) is added to milk, the casein precipitates, dragging some fat down with it. These are collected and used in the manufacture of cheese. Large amounts of casein are also used in the printing of wallpaper and fabrics, and for making artificial wool, glue, and plastic material similar to hard rubber. The liquid remaining after the separation of the casein and fat is known as whey. This contains the milk sugar, which is easily obtained in a pure state; it resembles sucrose in appearance, but is not so soluble and is only about one-fourth as sweet. The souring of milk is the result of the conversion of milk sugar into lactic acid, a liquid compound whose formula is $HC_3H_5O_3$. This change is known as lactic fermentation, and is brought about by certain bacteria. These bacteria (or their spores) are

everywhere present in the air, and are associated especially with dust and dirt. Sweet milk may be pasteurized; that is, it may be satisfactorily sterilized by being heated to about 65° for forty minutes, or to 95° for 5 minutes.

Maltose ($C_{12}H_{22}O_{11} \cdot H_2O$) · This sugar, also a disaccharide, is only about half as sweet as sucrose. It is prepared by the action of malt upon starch; hence the name maltose. It is an isomer of lactose.

Malt is the name applied to barley which has been moistened, kept in a warm place until it has germinated, and then heated until the vitality of the grain has been destroyed. In the process of germination a substance is formed known as diastase, and it is this substance which gives malt its property of changing starch into maltose. Ptyalin, in saliva, brings about a similar change in the starch present in our foods.

Starch ($(C_6H_{10}O_5)_x$ · Starch is called a polysaccharide because each molecule of starch contains many (26-30) monosaccharide units. It is one of the most abundant carbohydrates found in nature, and is especially abundant in seeds and tubers corn, wheat, potatoes, etc. (Fig. 30-2). Starch consists of minute granules which vary in size and characteristics according to their source.



Courtesy of the Corn Industries Research Foundation

Fig. 30-2. Diagram Showing the Structure of the Corn Kernel · Starch is the principal component, the kernel containing about 60 per cent of this substance. In the starch-manufacturing industry the gluten and the hulls are made into feed for livestock. The germ contains a high percentage of oil, which, after purification, is used for salad oils and vegetable shortenings

Starch dissolves only slightly in cold water; but in hot water its granules burst open, forming starch paste. Cold hydrochloric acid slowly converts starch into soluble starch. Iodine imparts a blue color to starch (p. 269), and this color change serves as a simple test for the presence of starch in foods.

Cellulose ($(C_6H_{10}O_5)_x$ · Cellulose also is a polysaccharide; it contains as many as 3000 monosaccharide units. Cellulose constitutes the main part of the cell walls of plants. Cotton is about 90 per cent cellulose; ordinary woods are from 40 to 65 per cent. The properties of cellulose can be judged by those of ordinary filter paper, which is nearly pure cellulose. It is insoluble in all ordinary solvents, but is readily converted into soluble derivatives. A cold, concentrated solution of sodium hydroxide gives a silk-like appearance to cellulose, and advantage is taken of this fact in the manufacture of *mercerized* cotton. Concentrated hydrochloric acid converts cellulose into glucose:

$$(C_6H_{10}O_5)_x + x\ H_2O \longrightarrow x\ C_6H_{12}O_6$$

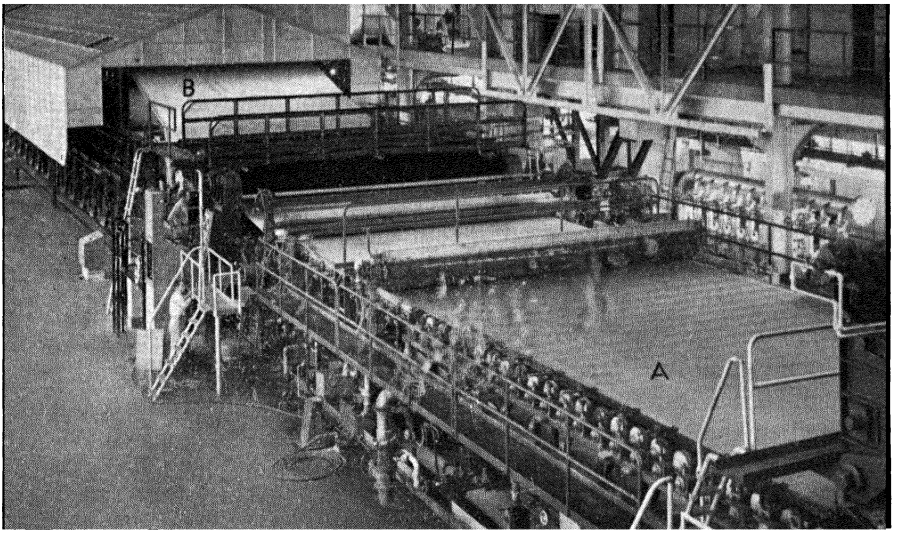


Fig. 30-3. View of the Interior of a Paper Mill In the figure, *A* is the traveling belt of wire cloth on which the wood fibers mat together to form the sheet. *B* is a sheet of paper in the process of drying

Paper · Paper is composed essentially of "a large number of small, hairlike cellulose fibers, matted and interwoven so closely that they form a continuous surface." The most expensive papers are made from cotton rags, but by far the greatest quantity of paper is made from wood pulp, the fiber of wood.

Briefly the method most largely used in the manufacture of paper is as follows: The pulp is first prepared by cutting the wood (mostly spruce, pine, hemlock, and balsam) into small chips, which are then "cooked" with a solution of calcium hydrogen sulfite or sodium hydroxide in order to remove the noncellulose portions. The product is next washed with water and bleached. The resulting pulp consists of wood fibers which are fairly pure cellulose. Certain substances, such as clay, alum, and resin, are then mixed with the pulp, the choice depending on the properties desired in the finished paper. The mixture of pulp, added substances, and water is next flowed onto a traveling belt of wire cloth in such a way as to form a sheet of paper (Fig. 30-3), from which the water is removed, first by pressure over endless woolen belts, and then by carrying the sheet around hot metal cylinders.

Cellulose Nitrates (Nitrocellulose); Cellulose Acetate · Cellulose contains a number of hydroxyl radicals. When the compound is treated with nitric acid containing some sulfuric acid, nitric acid esters of these

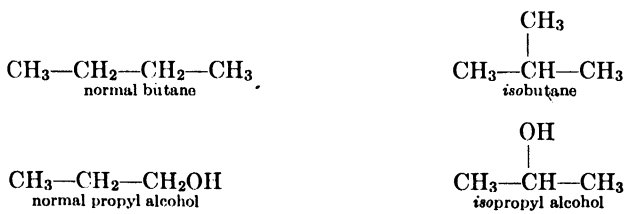
alcohol groups are produced, forming water and a mixture of covalent compounds called cellulose nitrates, but often known collectively as nitrocellulose. The sulfuric acid used along with the nitric acid assists the reaction by combining with the water formed. If the reaction is stopped before it is complete, the product contains from 10 to 12.5 per cent of nitrogen, and can be dissolved in a mixture of ordinary alcohol and ether to give collodion; if the action is continued, the nitrogen content of the product is increased, amounting to from 12.5 to 13.5 per cent. This product is insoluble in an alcohol-ether mixture, and is often referred to as guncotton. The cellulose nitrates are all inflammable, white solids, and under certain conditions are highly explosive.

When cellulose is treated with acetic anhydride, cellulose acetate is formed. This has many of the properties of cellulose nitrate, and is adapted to the same general uses. While it is more expensive than the nitrate, it has an added advantage for many purposes in that it is not so inflammable and is not explosive.

The Uses of Cellulose Nitrate · Cellulose nitrate has many uses, the most important of which are the following: (1) It is the chief constituent of smokeless gunpowder. (2) Photographic films are made from it, as well as from cellulose acetate. (3) It is the basic material in the lacquers that have come into such wide use in recent times, especially in the automobile industry. (4) Leatherlike products, used for bookbinding, automobile cushions, and handbags, consist of a canvas base (or other strong material) impregnated and coated with cellulose nitrate. (5) Collodion is a solution of cellulose nitrate in a mixture of alcohol and ether, and is used as a covering for wounds and as a base for fingernail polish.

Complex Molecules May Have Many Isomers · As the number of atoms in a molecule increases, the possible number of isomers also increases (p. 514). This is particularly true of polyfunctional molecules. We recognize several different kinds of isomers:

1. **Isomers formed by branching of chains or rings or moving functional groups along a chain.** For example, normal butane and isobutane are chain isomers; also normal propyl alcohol and isopropyl alcohol:



Ring isomers will be discussed in Chapter 31.

2. **Isomers containing different functional groups.** For example, ethyl alcohol and dimethyl ether are functional isomers:

$CH_3—CH_2—OH$ (ethyl alcohol) $\qquad$ $CH_3—O—CH_3$ (dimethyl ether)

3. **Geometrical isomerism, associated with a double bond.** Carbon atoms connected by a single bond are free to rotate. Hence two 1, 2-dichloroethanes cannot be obtained. But when two carbon atoms are connected by a double bond, rotation about the bonds cannot occur; and it is possible to have two isomers of a compound such as 1, 2-dichloroethylene. The isomers may be represented as follows:

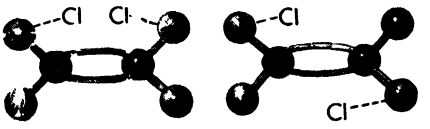
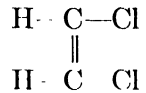
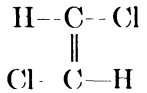


Fig. 30-4. Models of Cis and Trans Isomers



cis-dichloroethylene (where similar atoms are on the same side)



trans-dichloroethylene (where similar atoms are on different sides)

4. **Optical isomerism, involving an asymmetric carbon atom.** Optical isomerism is a type observed in many complex molecules and especially in carbohydrate molecules. This type of isomerism in carbon compounds is caused by the presence of a carbon atom that has four different atoms or groups attached to it. Such a carbon atom is called an asymmetric carbon atom. The presence of an asymmetric carbon atom in a molecule leads to a type of isomerism which involves "right-hand and left-hand" forms. Suppose, for example, that we have a compound in which a carbon atom, C, is attached to four different groups, W, X, Y, and Z (Fig. 30-6). Two models may be made, one of which is related to the other in the same way as the left hand is related to the right hand, or as the image of an object in a mirror is related to the object.

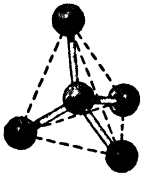


Fig. 30-5 · Model Showing Tetrahedral Bonds

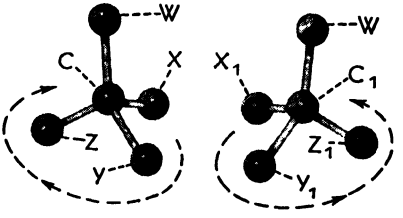


Fig. 30-6 · Right-Hand and Left-Hand Forms of an Asymmetric Molecule

As a specific example, let us take the compound lactic acid, $CH_3\text{-}\overset{*}{C}HOH—COOH$. Note that the carbon atom which is starred is

attached to $-CH_3$, $-H$, $-OH$, and $-COOH$, four different groups; and the molecule can theoretically exist in two forms, which are mirror images of each other. The two forms are represented conventionally as follows:



These two forms are exactly alike in such properties as freezing point, boiling point, density, and chemical reactions. The only difference in properties is in the different effects of the two forms on polarized light and in their reactions with other compounds which contain asymmetric atoms. These two forms are called optical isomers.

Polarized light is light which vibrates only in one plane. It can be produced by the reflection of ordinary light from a plane surface or by passing light through certain crystals. When such light is passed through a solution of one form of lactic acid, the plane of vibration of the light is twisted clockwise (to the right), and the solution is said to be dextrorotatory (*d*). Solutions of the other form of lactic acid will rotate the plane of polarized light counterclockwise. Such solutions are said to be levorotatory (*l*).

A compound whose solutions cause the plane of polarization to rotate is said to be optically active, and the presence of such optical activity is usually an indication that the compound contains an asymmetric carbon atom, although not all compounds with asymmetric carbon atoms are optically active.

When there is more than one asymmetric carbon atom in the molecule, the number of possible isomers increases. In general, the number of isomers will be 2^n, where n is the number of asymmetric carbon atoms.

There are sixteen aldohexose optical isomers, since there are four asymmetric carbon atoms in the aldohexose molecule (2^4) (p. 541). But there are only eight (2^3) ketohexose isomers (three asymmetric carbon atoms).

When we make a laboratory synthesis of a compound containing an asymmetric carbon atom, equal quantities of the *d*-form and the *l*-form will result, and the mixture (called a racemic mixture) is optically inactive.

Occurrence of Optically Active Compounds in Nature · It is of interest that compounds containing asymmetric carbon atoms are fairly common in nature, and almost always such compounds exist in an optically active form. Glucose, the sugar found in corn sirup and the most important of the sugars, is dextrorotatory. Of further interest is the fact that biological reactions are very sensitive to the configuration of the reacting

compounds: *d*-glucose will ferment, while *l*-glucose will not; *l*-adrenaline is forty times as active, physiologically, as *d*-adrenaline. It has been shown that all protein matter contains only the *l*-forms of the amino acids. This close relationship between optical activity and physiological properties, coupled with the difficulty of synthesizing one active form to the exclusion of the other, is one of the major problems in the preparation of medicinal products and other compounds such as the sugars.

Proteins

Proteins are the third major class of foods. They make up the muscle tissue, the skin, the hair, the nails, and the body cells of animals. Of the three major classes of foods, proteins are the most complex. In order to understand their composition and structure it will be helpful if we learn something about polyfunctional acids, particularly amino acids.

Polyfunctional Acids · Among the common polyfunctional acids, some of which are found in nature, are oxalic, lactic, aminoacetic (glycine), tartaric, citric, malic, and the chloroacetic acids. Their molecules contain at least two functional groups, at least one of which is an acid group.

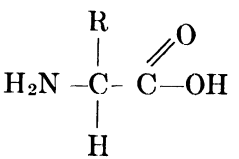
Oxalic Acid ($(COOH)_2$, *or* $H_2C_2O_4$) · This acid is found in many plants, including spinach and rhubarb. It is one of the products of the oxidation of ethylene glycol and also of sugar. Its chief use in industry is in bleaching and dyeing.

Lactic Acid (***Hydroxypropionic Acid***) ($CH_3—CHOH—COOH$) · This is the acid of sour milk. It is formed from milk sugar, called lactose, by lactic fermentation; the fermentation is caused by bacteria.

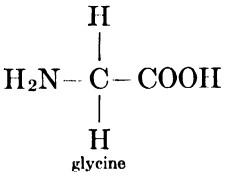
Tartaric Acid ($HOOC—CHOH—CHOH—COOH$, *or* $H_2C_4H_4O_6$) · This acid occurs in many fruits, especially in grapes. The tartrate salt $KHC_4H_4O_6$ is known as cream of tartar, and is used in the manufacture of some baking powders. $KNaC_4H_4O_6 \cdot 4\,H_2O$ is Rochelle salt; it is used in medicine (cathartic). Free tartaric acid is used in many soft drinks.

Citric Acid ($C_3H_4OH(COOH)_3$) · This acid is present in citrus fruits. Its magnesium salt is used as a laxative. The free acid is used in some soft drinks.

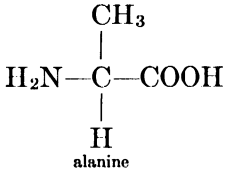
Amino Acids (***Amino Carboxylic Acids***) · These acids are important units of proteins. The general formula for an amino acid is



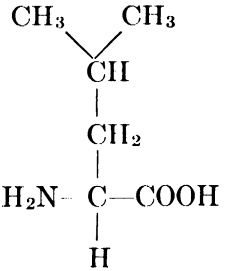
Amino acids contain the amino group ($-NH_2$) and the carboxyl group ($-COOH$); hence the name amino acid. These two groups are attached to a carbon atom which holds a hydrogen atom and another group, R. The R group, sometimes called the "tail" to distinguish it from the rest of the molecule, which is called the "head," is different in different amino acids. The formulas for several common amino acids are



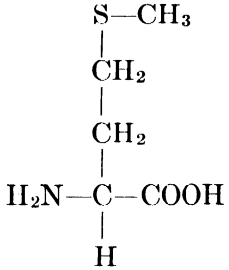
glycine



alanine



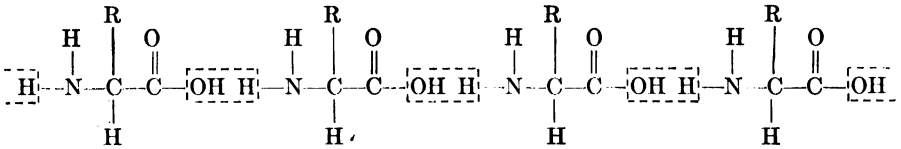
leucine



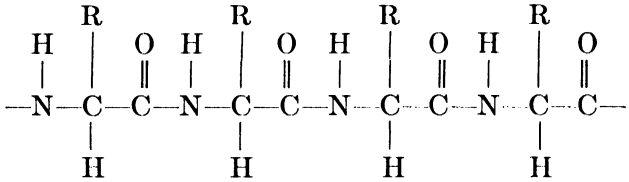
methionine

These amino acids are *alpha* amino acids, with the amino group attached to the first carbon atom next to the carboxyl group.

Proteins · Protein molecules, which are long-chain molecules, are made by a condensation of amino acids. The $-NH_2$ group in the "head" of one amino acid molecule reacts with the $-COOH$ group in the "head" of another amino acid molecule, splitting out water; and the residues then link together in a chain:



The resulting molecule has the structure



The bond between the amino acid residues (after water is split out) is called the "peptide linkage." The process of condensation of amino

acids may continue to form very long molecules of molecular weights varying from about 10,000 to 10,000,000 or more. These are the molecules of the natural proteins. The great variety of properties of the proteins, such as those of keratin in horn, hair, and wool, fibroin in silk, collagen in bones and connective tissues, albumin in egg white, zein in corn, glutenin and gliadin in wheat, and globulin in the blood, result from the particular kinds of amino acids present, as well as from their number and arrangement in the chain. Some more complicated proteins, such as hemoglobin and the nucleoproteins, contain also other groups, fastened to the "tails."

The amino acids are the units from which protein molecules are built. Protein materials, such as lean meat and cheese, when hydrolyzed in the presence of strong hydrochloric acid, yield a mixture of amino acids. This type of reaction is used to determine the structure and composition of proteins. Twenty-four amino acids—that is, amino acid molecules with twenty-four different kinds of "tails"—have been identified among the products of such hydrolysis. All the naturally occurring amino acids are optically active (p. 548) (the *l*-form), except the simplest one, glycine, which does not contain an asymmetric carbon atom.

Proteins are hydrolyzed in the digestive system, giving amino acids, which pass through the intestinal walls into the blood stream, and then are rebuilt by the various tissues into their characteristic proteins (p. 550), or oxidized to produce body energy.

Other Complex Organic Compounds

There are many other complex organic compounds in addition to fats, carbohydrates, and proteins. A discussion of them is beyond the scope of this book. However, our discussion of the approach we can make to understand the composition and structure of fats, carbohydrates, and proteins through their functional groups and types of reactions is a good illustration of the procedure followed by the organic chemist as he identifies complex organic molecules.

QUESTIONS

1. Define (*a*) *chain isomerism*; (*b*) *optical isomerism*; (*c*) *asymmetric carbon atom*; (*d*) *racemic mixture*; (*e*) *dextrorotatory*. What is (*f*) a polyfunctional molecule; (*g*) a trihydric alcohol; (*h*) a fat; (*i*) an amino acid; (*j*) a carbohydrate; (*k*) a monosaccharide; (*l*) nitrocellulose?

2. What effect is produced on the properties of an organic molecule when the same kind of functional group is increased in number? Use as examples C_3H_7OH, $C_3H_6(OH)_2$, and $C_3H_5(OH)_3$ (see page 169).

3. Distinguish between (*a*) an ester and a fat; (*b*) oleic acid and stearic acid; (*c*) butter and oleomargarine; (*d*) saponification and esterification; (*e*) a soap and the sodium salt of an acid such as acetic acid; (*f*) glycine and glycerin; (*g*) polarized light and a spectrum; (*h*) starch and cellulose.

4. (*a*) How would you prepare ethylene glycol from ethyl alcohol? (*b*) Write the equations for the series of reactions involved.

5. Write the formulas for the oxidation products of ethylene glycol. (Five different products are possible, without breaking the carbon chain.)

6. Write equations (*a*) for the partial and (*b*) for the complete esterification of ethylene glycol by acetic acid.

7. Write the equation for the esterification of glycerol (*a*) by acetic acid; (*b*) by stearic acid; (*c*) by nitric acid.

8. Write the equation for the saponification of the mixed ester of glycerol described in this chapter.

9. Give the relative advantages and disadvantages of each of the following as antifreeze agents: (*a*) methyl alcohol; (*b*) ethyl alcohol; (*c*) ethylene glycol; (*d*) glycerol.

10. Write the complete equation for the reaction that takes place in each of the following cases: (*a*) tartaric acid + potassium carbonate; (*b*) sodium stearate + magnesium sulfate; (*c*) olein + hydrogen; (*d*) alanine + ethyl alcohol.

11. Glucose can be readily oxidized to a monobasic acid and then to a dibasic acid. Write the structural formulas for these two acids.

12. The ketohexose whose formula is on page 541 can be esterified by acetic acid to form a pentacetate. Write (*a*) the equation for this reaction and (*b*) the structural formula of the pentacetate.

13. Which of the following compounds may have cis-trans isomers?

a. $CH_3—CH=CH—CH_3$

b. $CH_3—C(CH_3)=CH—CH_3$

c. $CH_2=CH—COOH$

d. $CH_3—CH_2—CH=CH—COOH$

14. The esterification of ethylene glycol by oxalic acid gives an ester which is a ring compound. What is the structural formula of this compound?

PROBLEMS

1. (*a*) One hundred grams of sucrose, when fermented, will yield how many grams of alcohol? (*b*) What volume of carbon dioxide, measured under standard conditions, would be formed at the same time?

2. (*a*) Calculate the weight of sodium hydroxide required to saponify 100 g of stearin. (*b*) What products would be formed? (*c*) Calculate the weight of each.

3. A volume of 200 ml of a 10 per cent solution of tartaric acid is exactly neutralized by a 10 per cent solution of sodium hydroxide. What volume of the latter is required?

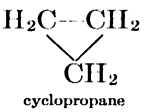
4. Calculate the percentage composition of sucrose

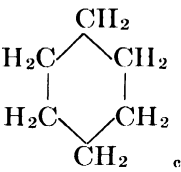
CHAPTER 31

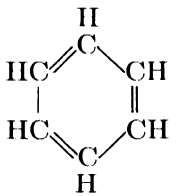
AROMATIC COMPOUNDS; CYCLIC COMPOUNDS

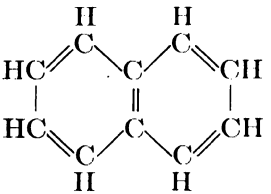
Coal Tar · The black, tarry substance, called coal tar, obtained by heating coal in the manufacture of coal gas and coke in the by-product coke ovens (p. 799) contains many useful substances, such as benzene, toluene, naphthalene, and phenol. These are obtained from the coal tar by fractional distillation, in a manner entirely analogous to that of the fractionation of petroleum (p. 802). Each of the compounds so obtained serves as the source material from which many other useful compounds are prepared. There are many thousands of these compounds; and all of them, whether obtained directly from coal tar or prepared from others so obtained, are known collectively as the coal-tar compounds.

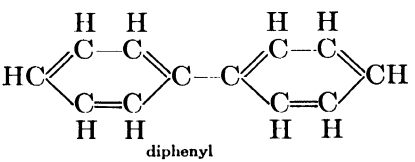
The annual production of coal tar averages about 750 million gallons. The organic compounds derived from coal tar are cyclic, or ring, compounds. There are many types of cyclic compounds; for example

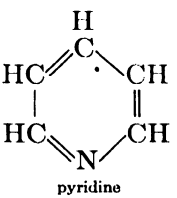

cyclopropane


cyclohexane


benzene


naphthalene


diphenyl


pyridine

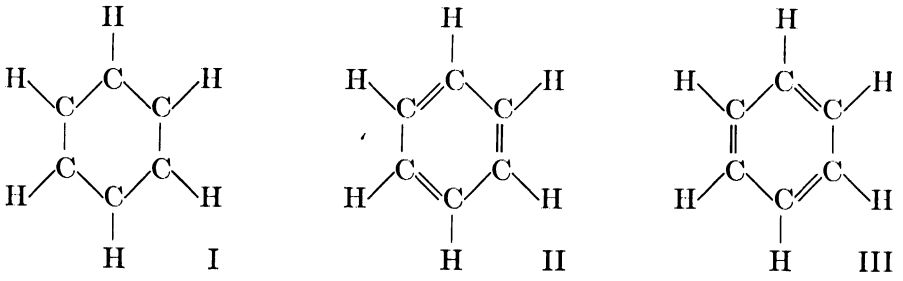
Of these six compounds, whose structural formulas are shown on page 553, the upper two are cycloparaffins. They belong in the saturated, or aliphatic, group of compounds, and are not found in coal tar. The last four are aromatic compounds. This name originally applied to their odor, but now denotes a particular structure, namely, ring compounds which have three alternating double bonds. Most aromatic rings are like those of benzene, napthalene and diphenyl; some, as in pyridine, have more than one kind of atom in the ring. Among the familiar aromatic compounds are aniline and the aniline dyes, trinitrotoluene (TNT), tannic acid and the tannins, and many medicinals, including aspirin, chloramine T, and the sulfa drugs. Many plastics, such as Bakelite and the glycerophthalates, are aromatic derivatives.

Just as the aliphatic compounds are derived from the methane series of hydrocarbons, so the aromatic compounds are derivatives of a series of hydrocarbons the simplest member of which is benzene (C_6H_6).

Benzene · This hydrocarbon is a colorless liquid which boils at 80.1°. It is highly inflammable, and is a good solvent for many organic compounds.

Benzene is the first member of a homologous series of hydrocarbons whose general formula is C_nH_{2n-6}. The second member, toluene, has the formula C_7H_8 or $C_6H_5CH_3$.

The proof of the structure of benzene provides one of the fascinating stories of organic chemistry. The great German chemist Kekule was the first to have the idea of the structure which was later proved convincingly, namely, that the benzene molecule is a flat, symmetrical, hexagonal ring of carbon atoms, with one hydrogen atom attached to each of the six carbon atoms (I):

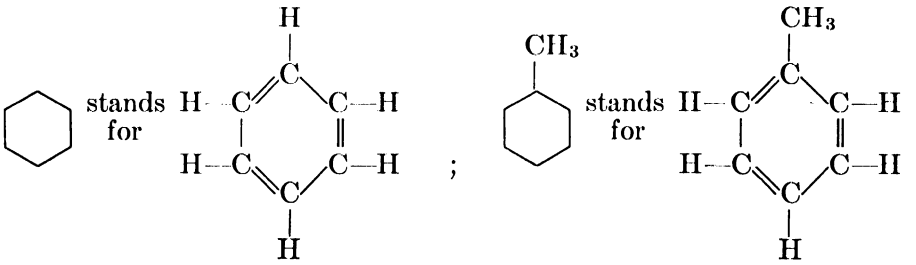


The fourth valence was accounted for on the theory that alternate double bonds are present (II). But according to modern theory we cannot write correctly a structural formula for benzene with single and double bonds, because the double bonds do not seem to be fixed in the positions indi-

cated in II. Formula III, for example, is also possible, and several others can be drawn, with valence bonds across the ring. In each of the formulas (II, III, and the others mentioned), the positions of the nuclei of the carbon and hydrogen atoms have not changed, and each carbon atom is tetravalent as required. The possibility of existing in several forms (by shifting electrons, not nuclei) leads to the condition which chemists call resonance (p. 348). In such cases the actual structure is not like any one of the possible structures, but is really a composite of all of them. Further, the molecule possesses an energy less than a molecule corresponding to any one of the possible structures would have. In general, this lower energy value due to resonance imparts stability to a molecule and lowers the reactivity. Resonance in benzene causes it to react like a saturated hydrocarbon toward many reagents.

A measure of the increased stability of benzene due to resonance may be obtained by considering the heat of reaction for the addition of one mole of hydrogen to a double bond. This reaction usually produces about 30,000 calories when an aliphatic hydrocarbon containing one double bond is saturated. If benzene had a structure corresponding only to II (or III), we should expect to find $3 \times 30{,}000 = 90{,}000$ calories evolved when the 3 double bonds are saturated. Actually only 49,000 calories are evolved. Further experiment shows that almost the whole of the difference appears in the hydrogenation of the first double bond which reacts; this requires the *addition* of 6,000 calories (endothermic reaction). Saturation of one of the double bonds destroys the resonance structure, since now two of the carbon atoms in the ring have two hydrogen atoms each, and are chemically different from the other four. The remaining double bonds hydrogenate as usual, producing 28,000 and 27,000 calories respectively. The resonance energy of benzene, therefore, is $30{,}000 - (-6{,}000) = 36{,}000$ calories.

It is convenient to write the formula for benzene as a hexagon:



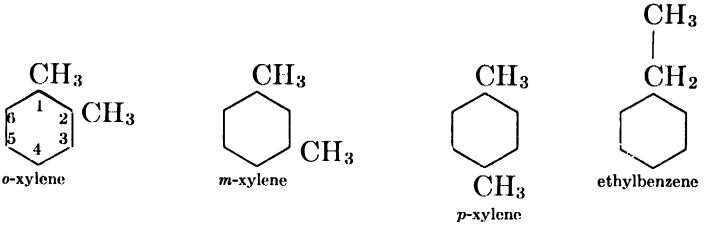
Homologues of Benzene · Toluene ($C_6H_5CH_3$) is methyl benzene; it occurs in coal tar. It may be synthesized by the action of methyl

chloride on benzene in the presence of anhydrous aluminum chloride as a catalyst:

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$$

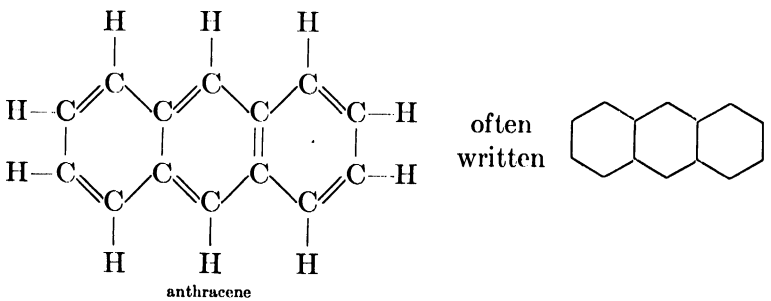
This type of reaction is called the Friedel-Crafts reaction, and it is employed in the synthesis of many organic compounds.

There are three dimethylbenzenes; they are called xylenes. Their structures are shown below, along with the homologue ethyl benzene, which has an ethyl group as the *side chain*, and which is an isomer of the dimethylbenzenes:



Naming the Positions in the Benzene Ring · In all disubstituted benzenes those with the two substituents on adjacent carbon atoms (1,2) are called ortho (*o*) derivatives; those in which the two substituents are attached to carbon atoms separated by one carbon atom (1,3) are called meta (*m*) derivatives; and the 1,4-substituted products are called para (*p*) derivatives.

Polycyclic Compounds · Aromatic compounds containing two or more rings are common. Most important of these is naphthalene, a white crystalline solid, commonly sold as moth balls. The structure of its molecule — a double ring, resembling a figure 8 — has already been given (p. 553). The structure of anthracene, a 3-ring molecule, is as follows:



Some of the polycyclic hydrocarbons or their derivatives with four, five, or more rings have been shown to produce cancer.

Reactions of Benzene and Its Homologues · Most of the derivatives of benzene and related aromatic hydrocarbons do not occur in nature

but must be prepared from the parent hydrocarbon. This is in contrast to the derivatives of the methane series of hydrocarbons, such as alcohols, organic acids, and carbohydrates, which are found in nature.

Although benzene is an unsaturated hydrocarbon, it usually appears, due to resonance (p. 555), to be saturated. Thus it reacts with chlorine by substitution rather than by addition at a double bond (pp. 515, 518).

$$C_6H_6 + Cl_2 \xrightarrow{\text{catalyst}} C_6H_5Cl + HCl$$

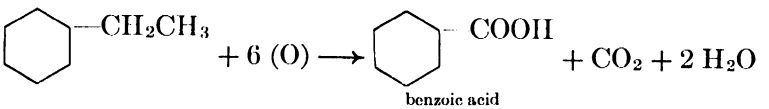
This reaction is catalyzed by metals like iron.

Under special conditions, such as in sunlight, benzene will add chlorine at the three double bonds to form $C_6H_6Cl_6$:

$$C_6H_6 + 3\ Cl_2 \xrightarrow{\text{sunlight}} C_6H_6Cl_6$$

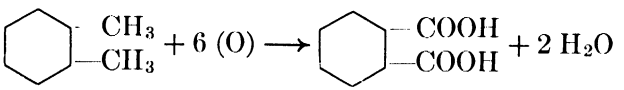
However, such additive reactions are unusual for benzene.

Derivatives of benzene which contain alkyl groups attached to the benzene ring may be oxidized by a strong oxidizing agent, such as chromic acid. When such oxidation occurs, the side chain, regardless of its nature, is changed to a carboxyl group. Thus ethylbenzene will give benzoic acid on oxidation:



benzoic acid

and *o*-xylene gives the important acid *o*-phthalic acid:



*ortho*phthalic acid

When benzene is heated with concentrated sulfuric acid, water is split out and a sulfonic acid results in which the sulfur is attached to a carbon atom:

$$C_6H_6 + HO—SO_2—OH \longrightarrow C_6H_5—SO_2—OH + H_2O$$

benzenesulfonic acid

Benzenesulfonic acid is nearly as strong as sulfuric acid.

When benzene is treated with strong nitric acid in the presence of a dehydrating agent, such as sulfuric acid, nitro compounds are formed, in which the nitrogen atom is directly attached to a carbon atom:

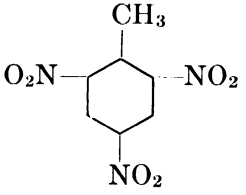
$$C_6H_6 + HO—NO_2 \longrightarrow C_6H_5NO_2 + H_2O$$

nitrobenzene

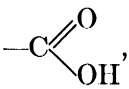
With fuming nitric acid two or three nitro groups enter positions meta to each other. Nitrobenzene, a pale-yellow, oily liquid which boils at

211°, is used in the preparation of aniline, which, in turn, is used in making aniline dyes and many other products.

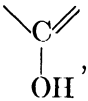
Toluene can be nitrated readily. The first nitro group enters a position ortho or para to the methyl group. Further nitration yields 2, 4, 6-trinitrotoluene, which is the powerful explosive known as TNT.



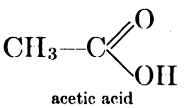
Phenols · The phenols are aromatic hydroxy compounds in which the hydroxyl group is directly attached to a carbon atom belonging to the ring. They are different from alcohols in that they are definitely acidic. Their acidity is in agreement with the general statement that a hydrogen atom attached through an oxygen atom to a carbon atom which has a double bond will be acidic (p. 529); this is true for the carboxyl group,



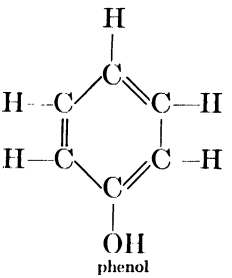
, and for the phenolic group,



, as shown here by the formulas for acetic acid and phenol:



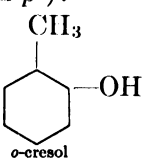
acetic acid



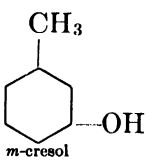
phenol

However, hydroxy compounds which have the hydroxyl groups in the side chain do resemble the aliphatic alcohols. Such a compound is benzyl alcohol ($C_6H_5CH_2OH$).

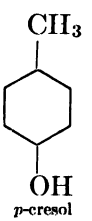
Phenol itself (C_6H_5OH), also called carbolic acid, is a crystalline compound slightly soluble in water. The hydroxytoluenes are called cresols (*o*-, *m*-, and *p*-):



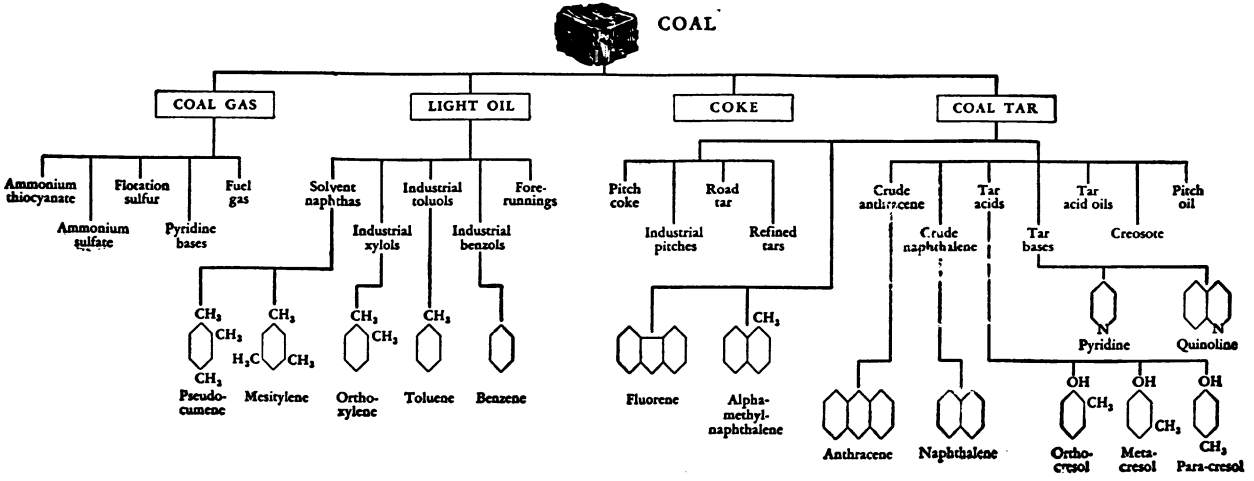
o-cresol



m-cresol



p-cresol



Koppers Company

Fig. 31-1. A Few of the Many Products Obtained from Coal

The phenols are generally excellent antiseptics, phenol being used as a standard with which all other antiseptics are compared. The term phenol coefficient of an antiseptic means the measure of its efficiency as compared with phenol. Phenol and the cresols have a very irritating action on the skin and are highly poisonous.

Phenol and the cresols are found in coal tar, but may be readily synthesized; one method is to prepare the salt of the appropriate sulfonic acid and fuse it with sodium hydroxide:

$$C_6H_5—SO_2—ONa + NaOH \longrightarrow C_6H_5OH + Na_2SO_3$$

A more recently developed method, which gives promise of being very successful, is the catalytic vapor-phase hydrolysis of monochlorobenzene.

Chemical Reactions of Phenols · In its chemical reactions phenol is a weak acid. It will form salts with bases:

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

Phenols are much more reactive than benzene itself, and are readily chlorinated, brominated, nitrated, or sulfonated.

Polyhydric Phenols · Just as many alcohols contain more than one hydroxyl group (ethylene glycol and glycerol) and many other compounds contain alcoholic hydroxyls in addition to other reactive groups (hydroxy acids, carbohydrates, etc.), so we may have polyhydric phenols and other derivatives containing phenolic hydroxyls. The formulas of some of these compounds are shown on page 561.

Aniline · When nitrobenzene is reduced, it is changed to an ammonia analogue called aniline:

$$C_6H_5NO_2 + (6\ H) \longrightarrow \underset{\text{aniline}}{C_6H_5NH_2} + 2\ H_2O$$

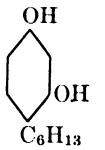
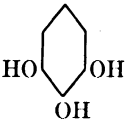
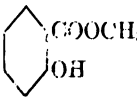
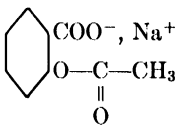
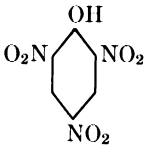
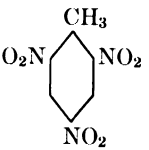
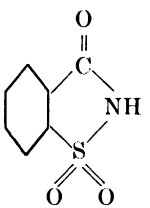
Aniline may be prepared also by treating the sodium salt of benzenesulfonic acid with sodamide ($NaNH_2$) or ammonia.

Aniline is an oily liquid, only slightly soluble in water. It boils at 180°. It undergoes reactions with acids to form crystalline salts:

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_3^+, Cl^-$$

This is a characteristic reaction of amines. Aniline and other aromatic amines are sensitive to oxidation, turning dark in the presence of air. The diamines are used as reducing agents (developers) in photography; *p*-phenylenediamine (*p*-diaminobenzene) in particular is much used for this purpose. Aniline will react with acetic anhydride or acetyl chloride or, under suitable conditions, even with acetic acid to form acetanilide:

$$C_6H_5—NH_2 + CH_3COOH \longrightarrow \underset{\text{acetanilide}}{C_6H_5—NH—CO—CH_3} + H_2O$$

 Hydroquinone. A powerful reducing agent, it is used as a photographic developer.	 Hexylresorcinol. It is used in medicine as an antiseptic.	 Pyrogallol. It is used to absorb oxygen in analysis of gas mixtures, and as the photographic developer "pyro."
 Salicylic acid.	 Methyl salicylate, oil of wintergreen.	 Aspirin, a phenolic ester of acetic acid.
 Picric acid, a strong acid formed by nitration of phenol. Yellow, it is used as a dye; also as an explosive.	 Trinitrotoluene, TNT, a violent explosive, though sluggish and not easily detonated (see page 600).	 Saccharin, a sugar substitute. The more soluble sodium salt, formed by replacing the hydrogen on the group $>NH$, is generally used.

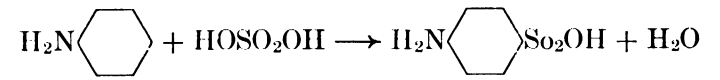
Acetanilide ($C_6H_5—NH—CO—CH_3$) · Acetanilide is a crystalline compound used in headache powders and for the treatment of fevers, since it has the effect of lowering body temperature. It is sometimes slightly toxic, so that other derivatives, such as aspirin, are rapidly supplanting it. Acetanilide is used instead of aniline as an important intermediate in the preparation of many organic compounds because aniline itself is so sensitive to oxidation and decomposition that it is not suitable for many organic reactions. By changing aniline to acetanilide and then carrying out further reactions, one can "protect" the amino group, so that no decomposition takes place during the reaction. The amine group may then be restored by treating the compound with bases:

$$C_6H_5NHCOCH_3 + NaOH \longrightarrow C_6H_5NH_2 + CH_3COONa$$

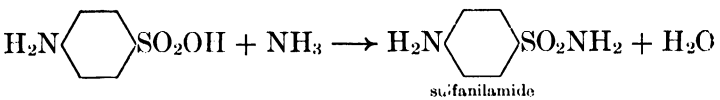
Secondary and Tertiary Amines · Secondary and tertiary amines are prepared by replacing successively two and all three of the hydrogen atoms of ammonia with alkyl or aromatic groups. The most important amines of these types are methylaniline (methylphenylamine) and dimethylaniline (dimethylphenylamine): $C_6H_5—NHCH_3$ and $C_6H_5—N(CH_3)_2$. These amines are useful intermediates in the preparation of dyes and some of the sulfa drugs. They are more resistant to oxidation and other types of decomposition than aniline is, and therefore undergo chemical reactions more smoothly than does aniline.

Among the most interesting reactions of aniline and the methylanilines are those involving the *p*-hydrogen atom. The presence of an amino or substituted amino group appears to activate the *p*-hydrogen atom (and the *o*-hydrogen atom), so that it is easily replaced by other groups. This is illustrated by the method of synthesis of sulfanilamide, one of the earlier developed therapeutic agents.

Sulfanilamide Synthesis · Aniline is readily sulfonated by treatment with sulfuric acid to form sulfanilic acid (*p*-amino benzene sulfonic acid),



which can, in turn, by suitable treatment with ammonia, be changed to sulfanilamide:



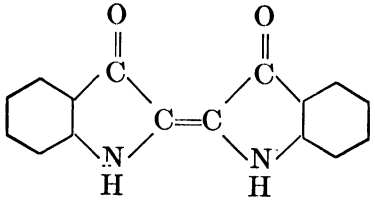
Diazotization · A very important reaction of the aromatic amines is diazotization, in which the amine is treated with nitrous acid in the presence of hydrochloric acid:

$$C_6H_5NH_2 + HONO + HCl \longrightarrow C_6H_5N_2Cl + 2\ H_2O$$

The diazo (two-nitrogen-atom) compounds are of great importance in the preparation of aniline dyes (see below). They undergo many other chemical reactions, which make them perhaps the most versatile organic intermediates.

Coal-Tar Dyes · All dyes prepared from compounds present in coal tar are known as *coal-tar dyes* or *aniline dyes*. Many hundreds of these dyes have been prepared, of every imaginable color. Two of the most common of these, *indigo* and *alizarin*, were formerly obtained from vegetable sources only. Later, chemists found out how to make them in the laboratory, and now they are made in this way at a lower cost than they can be obtained from natural sources.

Most of the coal-tar dyes are very complex compounds; for example, indigo has the following structural formula:



Historical. The first aniline dye was made in 1856 by an English boy eighteen years of age. His name was William Perkin. The boy was assisting in the laboratory of an English university, and during the holidays he spent his time in trying to make *quinine*. In the course of some experiments with aniline he noticed that a colored substance of great beauty was produced. Perkin got the idea that perhaps this new compound, which he had prepared from aniline, might be used as a dye. He finally succeeded in showing that it could be so used, and that it was superior to vegetable dyes in coloring power. This discovery led to others; and the investigation continues, as shown by the fact that our dye factories employ hundreds of chemists. It is of interest to note that in 1906, fifty years after Perkin's discovery, he came to the United States and attended a great meeting held in New York City in honor of the fiftieth anniversary of the discovery of the first aniline dye.

Color and Chemical Constitution; Dyes

Theory of Color · Light which is visible to the eye is made up of a mixture of wave lengths of light varying from about 4000 Å to about 8000 Å. In this range are found all the seven primary colors of the rainbow, namely, violet, indigo, blue, green, yellow, orange, red. All these colors, mixed together, give white light; but if any one of them is removed, what is left is colored light, complementary to the color removed.

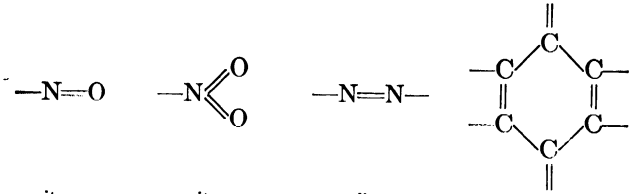
In general, the color of a substance is due to the light that it absorbs. If it absorbs white light completely, it is black. If it absorbs certain wave lengths of light and reflects or transmits others, it has the color of the light it reflects or transmits. The color of the light reflected or transmitted is complementary to the color of the light absorbed. The following colors are complementary:

COLOR OBSERVED	COLOR ABSORBED
Violet	Green-yellow
Indigo	Yellow
Blue	Orange
Blue-green	Red
Green-yellow	Violet

The color of organic compounds is closely associated with the structure of the molecules. The absorption of light waves by molecules is related to the vibration frequency of the electrons that bind the atoms together in the molecules.

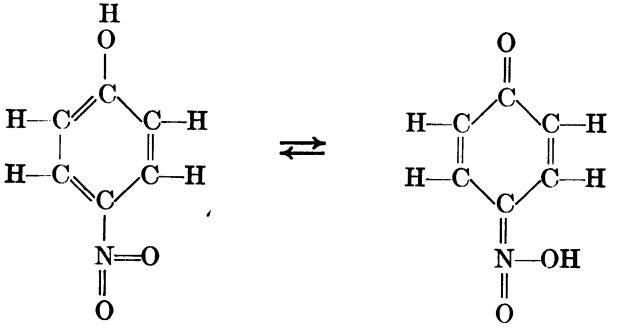
Chromophore Groups · In order to absorb visible light an organic compound must contain one or more atomic groups called chromophores. These chromophores are invariably groups containing double bonds. In such double bonds the electrons are bound relatively loosely and hence vibrate at such relatively low frequencies that they can absorb light somewhere in the visible part of the spectrum. Electrons in the tighter bonds absorb light waves in the ultraviolet region.

Among the most important chromophores are the following:



nitroso group | nitro group | diazo group | quinonoid group

An example of the effect of the chromophore is to be found in *p*-nitrophenol. Phenol is colorless, but *p*-nitrophenol is colored. It is interesting to note that *p*-nitrophenol will undergo a molecular rearrangement consisting of a migration of the hydrogen atom of the hydroxyl group to an oxygen atom of the nitro group, with an accompanying shift of double bonds:



nitrophenol (phenolic form) ⇄ nitrophenol (quinonoid form)

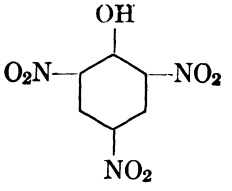
Many colored organic molecules contain such a set of double bonds, known as the quinonoid group.

Colorless compounds which contain chromophore groups may often be made to absorb visible light, or the color of a dye may be *changed*, by introducing other groups or atoms into the molecules. For example,

fluorescein, which is an orange powder, may be brominated to tetrabromofluorescein (eosin), which is used in making red ink. Usually any increase in molecular weight produces a darker color.

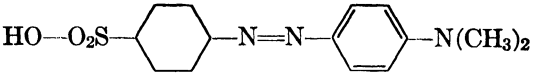
Auxochromes · Many colored organic molecules do not make satisfactory *dyes*, because they will not fasten themselves to a fiber. In order to change a colored compound to a dye some group must be introduced which will react with the fiber to fix the dye. Among such groups, called auxochromes, are the phenolic group (OH) in acid dyestuffs and the amino group ($-NH_2$) in basic dyestuffs. The following are some of the classes of dyes and coloring matters:

1. **Nitrophenol dyes.** Paranitrophenol has just been described. Picric acid,

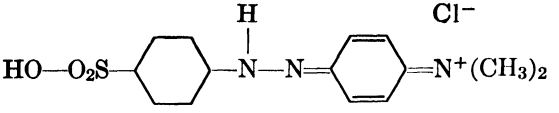


shows the same type of hydrogen migration as is shown by nitrophenol (p. 564).

2. **Azo dyes.** These dyes are made by coupling diazonium salts with phenols or amines. The common indicator methyl orange, for example, can be made by diazotizing sulfanilic acid and then coupling the resulting diazonium salt with dimethylaniline. Its formula is



In the presence of hydrochloric acid methyl orange shifts to a form which contains the quinonoid group:



3. **Phthalein dyes.** Such dyes are made by the reaction of phenols or amines with phthalic anhydride. Fluorescein is made, in a similar way, by the condensation of phthalic anhydride with resorcinol. The color of fluorescein is so intense that a small amount of it will color a large quantity of water. It has been used to color the water surrounding lost airmen in order to show where they are located. Many of the dyes are derivatives of naphthalene or anthracene. In general, the naphthalene

dyes are darker than those derived from benzene, because of their greater molecular weight. Many other classes of dyes exist, and their variety is limited only by the imagination of the research chemist.

QUESTIONS

1. Define (*a*) *auxochrome group;* (*b*) *chromophore group;* (*c*) *benzene ring;* (*d*) *ortho, meta,* and *para positions;* (*e*) *phenol coefficient.* What is (*f*) a dihydric phenol; (*g*) a primary amine; (*h*) an azo dye; (*i*) a phthalein dye.

2. (*a*) How do you account for the fact that the hydrogen of the OH group in phenol and in acetic acid ionizes in water solution? (*b*) Why does an alcohol not form acid solutions in water?

3. What is the relationship between (*a*) aromatic compounds and the structure of graphite; (*b*) aliphatic compounds and the structure of diamond?

4. (*a*) Give the names, structural formulas, and uses of ten common aromatic compounds. (*b*) Do these uses depend upon the property of some functional group in the molecule?

5. Can you name three ways in which aromatic compounds differ from aliphatic compounds?

6. Write the structural formula of (*a*) isopropylbenzene; (*b*) 2, 4-dihydroxytoluene.

7. What is the relationship between the structure of an organic molecule and its color?

8. (*a*) What is meant by the term *resonance*? (*b*) In terms of resonance, explain the fact that benzene does not react readily by addition.

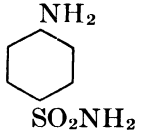
CHAPTER 32

SOME NATURAL PRODUCTS AND SYNTHETICS

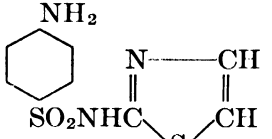
Introduction · For thousands of years man has used materials found in nature to provide himself with food, clothing, shelter, fertilizers, and drugs. Careful studies have revealed the structure and properties which characterize the materials used for these various purposes. With this information the chemist has synthesized products which are identical with or, in many cases, better than the materials found in nature. He has been able to duplicate or simulate many of the natural vitamins and drugs; he has made new anesthetics, new antiseptics, new fibers, and insecticides; he has learned to separate the molecules in petroleum and re-form them into improved gasolines, or to polymerize them into rubber, plastics, and textiles. Much of the luxury and improved standard of living in our modern life, as compared with that of ancient peoples, is the result of the work of the chemist.

Drugs and Pesticides · One of the great contributions of the chemist is that of improving the health conditions of the world. To do this he has developed better drugs and pest killers. A few of the better-known drugs, insecticides, and specifics will be described here.

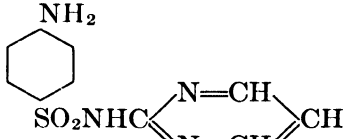
The Sulfa Drugs · Within very recent years a group of chemicals known as the sulfa drugs have been synthesized and found to be specifics for a number of common infections. They were found to be particularly useful in combating those bacteria that produce pneumonia, gas gangrene, meningitis, and blood poisoning. The first of these compounds prepared was sulfanilamide (below), but it caused serious reactions in some patients. Chemists modified the properties of the sulfa drugs by replacing one of the hydrogen atoms on the $-SO_2-NH_2$ group of sulfanilamide with other groups, producing compounds that are more effective in combating bacteria, but less harmful to the patient. Two of the more common sulfa drugs are sulfadiazine and sulfathiazole.



sulfanilamide

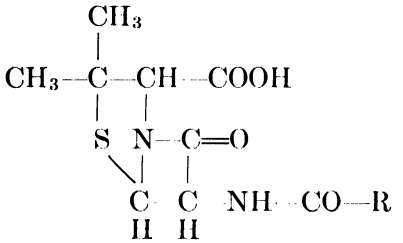


sulfathiazole



sulfadiazine

Antibiotics · Close upon the development of the sulfa drugs came the discovery of penicillin, which has proved to be extremely effective in the treatment of gonorrhea, pneumonia, meningitis, osteomyelitis, gas gangrene, and streptococcus and staphylococcus infections. Penicillin is called an antibiotic agent; it inhibits or kills microörganisms. It is produced by various strains of mold called *Penicillium notatum*, and is now prepared on a large scale. Penicillin has been synthesized. The general formula for penicillin is



R may be

$-CH_2-CH{=}CH-CH_2-CH_3$

$-CH_2-C_6H_5$

$-CH_2-C_6H_4-OH(p)$

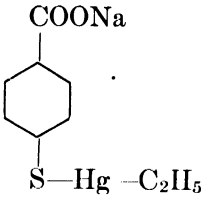
$-CH_2-(CH_2)_5-CH_3$

Some other antibiotics now used are streptomycin, chloromycetin, and aureomycin.

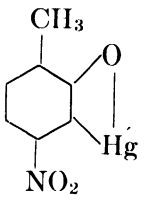
Alkaloids · A number of very important drugs are obtained from plants and trees. Some of these belong to the group known as alkaloids. The most common of these are quinine (an antimalarial); morphine and cocaine (narcotics); digitalis, strychnine, and caffeine (heart stimulants); and atropine (which dilates the pupil of the eye). Most of the alkaloids are very poisonous.

Quinine, Atabrine, Aralen · Quinine has long been known as an effective drug in the treatment of malaria. It has been obtained from the bark of the cinchona tree, grown chiefly in Java. Quinine has been synthesized; the process is not yet a commercial one. Two other compounds, Atabrine and Aralen, also effective in the treatment of malaria, have been synthesized and are now available. It is said on good authority that Aralen is a perfect cure for malaria.

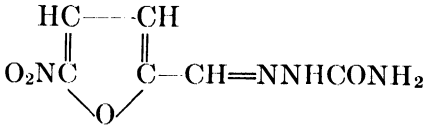
Antiseptics · Some of the better-known chemicals that are or have been used as antiseptics or germicides are hydrogen peroxide, boric acid, mercuric chloride, phenol, Mercurochrome, and iodine. Many of the older antiseptics have been replaced by new ones, such as Argyrol, Merthiolate, Phemerol, Furacin, and Metaphen, which have more potent bactericidal activity or are less harmful to the patient.



Merthiolate



Metaphen

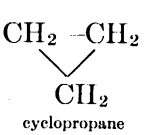


Furacin
(with 5-membered ring)

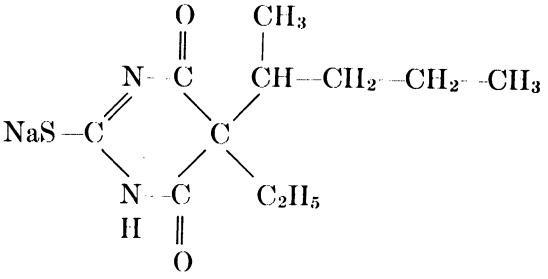
Anesthetics · The use of anesthetics in surgery (ether was introduced in 1842), as well as the use of antiseptics, has greatly increased the possibilities of successful surgery. Of the many local anesthetics there are the older drugs cocaine and Novocain and the more recent ones Pontocaine and Nupercaine. Nupercaine shows a great deal of promise because of its prolonged effect.

Several general anesthetics are ether ($C_2H_5OC_2H_5$), chloroform ($CHCl_3$), nitrous oxide (N_2O), and cyclopropane.

Pentothal Sodium is an intravenous type of anesthetic. It acts quickly, and the patient recovers from it soon.



cyclopropane

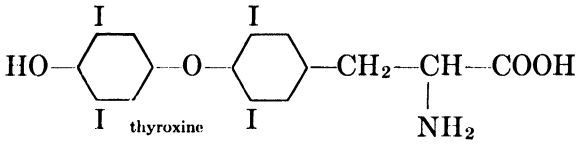


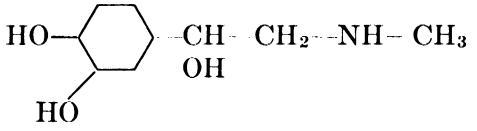
Pentothal Sodium

Hormones · The hormones are organic substances secreted by the ductless glands into the blood or lymph. They are then carried to other parts of the body. Hormones are frequently called body-regulators; the proper amounts of different hormones are essential for normal body functions.

Adrenaline (p. 570) was the first hormone to be isolated. It is produced in the adrenal glands, located at the upper poles of the kidneys. It has a powerful stimulating action on the sympathetic nerve endings. As a medicine, it is used to cause contraction of the blood vessels.

Thyroxine (p. 570) is the component of the thyroid hormone which gives this hormone its activity. It is produced in the thyroid glands and accelerates cellular metabolic processes. It is an amino acid (p. 549).



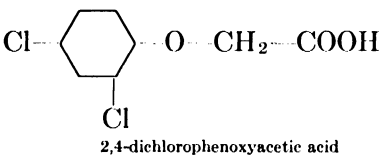


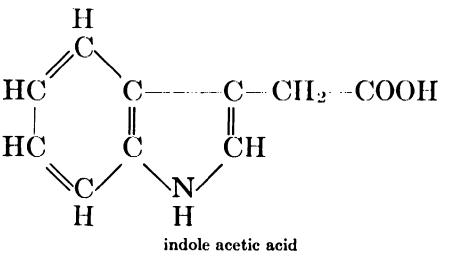
In regions where the drinking water is deficient in iodine, the thyroid glands may produce insufficient thyroxine, causing serious bodily disorders.

Insulin was discovered by Banting in 1923. It is a protein of known structure in the pancreas. A deficiency of this hormone leads to diabetes; this condition may be corrected by the injection of insulin.

A variety of hormones is produced in the pituitary glands. These hormones seem to regulate the action of the other ductless glands.

Plant-Growth Stimulants · Plant growth is controlled by substances that have become known as plant hormones. Various synthetic materials will produce stimulating effects similar to the natural ones. Among these are vitamin B_2 and indole acetic acid, which are potent root stimulants. A chemical which stimulates abnormal growth and finally causes the death of certain plants is 2,4-dichlorophenoxyacetic acid. It is commonly called 2,4-D and is sold on the market as a weed-killer.





Foods

Foods supply the building materials for growth and the materials for the repair of tissues and for the synthesis of the various chemical substances that are involved in body processes. From foods we obtain also the energy required by our bodies.

Composition of Foods · The compounds present in our foods are very numerous, and often exceedingly complex in structure, but they may all be placed in one or more of the following general classes:

1. **Proteins.** Proteins (p. 549) are everywhere abundant in animal and vegetable organisms, and constitute the principal part of the tissue of the living cell. The casein of milk, the gluten of flour, and the albumin of egg are proteins. All the proteins contain nitrogen, carbon, hydrogen, and oxygen, and some contain also sulfur, iodine, and phosphorus. Very small percentages of other elements are present in certain proteins; thus, hemoglobin, which is present in blood, contains iron.

2. **Fats.** These consist of a mixture of the glyceryl esters of certain acids (p. 536).

3. **Carbohydrates.** This group includes the sugars, starches, and related compounds (p. 540).

4. **Mineral matter.** Certain compounds of the metals, such as calcium phosphate, sodium chloride, and the iron salts, are also needed.

5. **Water and oxygen.** Though we do not usually speak of water and oxygen as foods, nevertheless both are essential to life, and they deserve to be called foods in the true sense of the word.

6. **Vitamins.** The vitamins, usually considered to be foods, will be discussed in a later section of this chapter.

Functions of Different Food Materials · Of the carbohydrates the sugars are most readily assimilated. They are oxidized in the body, for the most part in the muscles, and yield energy directly and quickly. The starches are hydrolyzed in the digestive system in the presence of enzymes into sugar (glucose).

The fats are converted partially or completely into glycerol and fatty acids in the presence of enzymes during digestion. The products are absorbed through the wall of the small intestine into the blood, and rebuilt into the body's characteristic fats. The body fats may be oxidized, giving heat, but more slowly than the sugars. Fats are stored in adipose tissue, and are important constituents of various tissues. Some of the sugars are changed into fats.

The proteins, made up of long, high-polymer molecules, as we have previously noted (p. 550), are hydrolyzed into amino acids in the stomach, in the presence of hydrochloric acid and the enzyme pepsin, and in the upper intestine in the presence of the enzymes trypsin and erepsin. These catalysts make possible the digestion of a meal of proteins within a few hours instead of several months. After the amino acids have been split out of the proteins, they are absorbed through the intestinal wall and carried by the blood to all parts of the body; the various tissues then select the proper amino acids and build them into protein tissues, such as skin, hair, fingernails, muscle fibers, and nerves. Body proteins may also serve as a source of energy, by oxidation, if the amounts of sugars

AVERAGE COMPOSITION OF SOME COMMON FOODS*

KIND OF FOOD	WATER %	PROTEIN %	FAT %	CARBO HYDRATES %	ASH %	FUEL VALUE, kcal/100 g
Apples (fresh, all)	84.1	0.3	0.4	14.9	0.29	64
Beans (dried)	12.0	25.1	1.8	57.7	3.4	347
Beef (round, medium)	67.0	19.3	13.0	0.0	0.95	194
Bread (white, all-milk)	36.0	9.0	3.6	49.8	1.6	268
Butter	15.5	0.6	81.0	0.4	2.5	733
Corn (sweet)	73.9	3.7	1.2	20.5	0.66	108
Eggs	74.0	12.8	11.5	0.7	1.0	158
Ham (lean, smoked)	49.0	19.5	25.0	0.0	5.8	304
Lettuce (fresh)	94.8	1.2	0.2	2.9	0.91	18
Milk (cow, fresh)	87.0	3.5	3.9	4.9	0.7	69
Oatmeal (uncooked)	8.3	14.2	7.4	68.2	1.9	396
Olive oil	0.0	0.0	100.0	0.0	0.0	900
Oranges (fresh)	87.2	0.9	0.2	11.2	0.47	51
Peas (green)	81.4	5.4	0.3	12.1	0.77	73
Potatoes (fresh)	77.8	2.0	0.1	19.1	0.99	85
Rice (white, uncooked)	12.3	7.6	0.3	79.4	0.4	351
Spinach	92.7	2.3	0.3	3.2	1.53	25
Tomatoes (fresh, red)	94.1	1.0	0.3	4.0	0.57	23
Wheat flour (white)	12.0	9.3	1.0	77.2	0.5	355

*From Circular No. 549, United States Department of Agriculture.

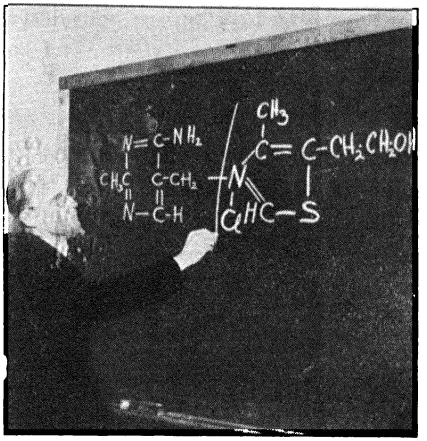
and fats in the body fall below certain levels, as during starvation or partial starvation.

The food minerals supply the ions that are important in body processes: Ca^{++} and PO_4^{---} in building bones and teeth; Ca^{++}, Na^+, and K^+ in muscular action; Na^+, Cl^-, HCO_3^-, CO_3^{--}, $H_2PO_4^-$, and HPO_4^{--} in the regulation of the *p*H of the blood and in the carbon dioxide–oxygen exchange between blood and lungs; Fe^{+++} for the hemoglobin of the red blood cells; and F^-, I^-, etc. (pp. 263, 264) for other functions.

The Calorific Value of Foods · Energy is supplied to the body, as has already been noted, by the oxidation of food materials to carbon dioxide and water. Oxygen absorbed from the lungs by the red corpuscles of the blood is the oxidizing agent. The yield of energy, or the calorific value, of carbohydrates, fats, and proteins, as determined in a calorimeter (p. 584) and in actual combustion in the body, is (on the average) as follows:

	CLASS OF FOODS	KILOCALORIES PER GRAM	KILOCALORIES PER POUND
ENERGY VALUES OF SEVERAL CLASSES OF FOODS	Carbohydrates	4	1815
	Fats	9	4082
	Proteins	4	1815

An individual's food requirements, from the standpoint of calorific value, vary with conditions, such as body weight, age, occupation, and climate. For an adult living an ordinary life in a temperate climate, and not engaged in manual work, 2400 kcal are sufficient. If one is engaged in muscular work, 75 to 300 kcal in addition are needed per hour of work, according to how much work is done.

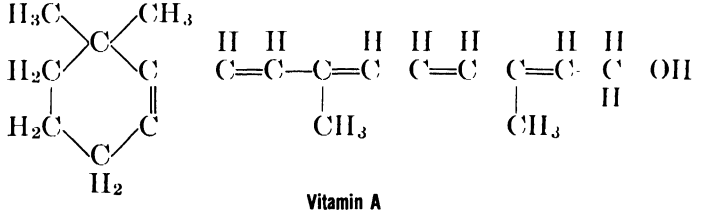


Merck & Co. Inc.

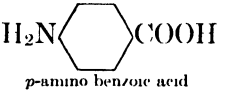
Fig. 32-1. Most of the Vitamins Have a Complex Structure. The figure shows the distinguished chemist Dr. R. R. Williams explaining the structural formula of vitamin B_1, which he had determined. After the structural formula of a compound is determined, chemists are generally able to work out a method for synthesizing the compound.

Vitamins. Until about 1913 it was generally believed that proteins, carbohydrates, fats, and mineral matter (p. 32) constituted a complete diet. But since that time systematic experimental studies have shown that these substances, if highly purified, will not maintain the health of man and of the animals, and that natural foodstuffs, which have not been purified, contain certain other substances absolutely essential to growth and health. These substances, usually present in relatively minute amounts in materials that we use as foods, we call vitamins. Systematic research has now led to the identification and isolation of more than a dozen vitamins.

The vitamins were originally designated by letters (vitamin A, B, C, etc.) before their chemical identity was established. Now we know the chemical formulas for many of them and we find that some have simple and others relatively complex structures. For example:

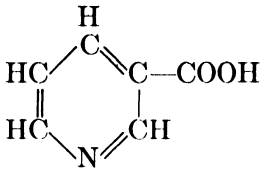


Vitamin A



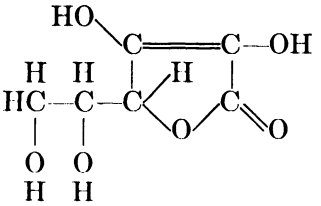
p-amino benzoic acid

A Vitamin of the B Complex



nicotinic acid

Another Vitamin of the B Complex



ascorbic acid

Vitamin C

Several of them have been synthesized; the others are isolated from natural products.

VITAMINS

LETTER		NAME OF CHEMICAL OR CHARACTERISTIC	MAINLY USED FOR	MAINLY FOUND IN
A		a carotene	ophthalmia, general weakness	cod-liver oil, some greens, liver, vegetables
B COMPLEX	B_1	thiamin	growth, beriberi	wheat germ, yeast
	B_2 (G)	riboflavin	growth, general health	yeast (brewers'), liver, milk
	B_3 (P-P)	nicotinic acid or niacin	growth, pellagra	liver, wheat germ
	B_4	pantothenic acid	antidermatitis	liver, yeast
	B_5	folic acid	fertility, hatchability	liver
	B_6	pyridoxin	growth	wheat germ, yeast
	B_{12}	complicated ring structure containing cobalt	prevention of pernicious anemia	microörganisms during fermentation
C		ascorbic acid	scurvy	vegetables, citrus fruit juice
D		a sterol	general resistance	cod-liver oil
E		several tocopherols	fertility	vegetable oils
H		biotin	growth producer	yeast, some seeds
K		a hydrocarbon derivative	coagulation of blood	vegetables

Production of vitamins by synthesis (A, B_1, B_2, B_3, B_4, B_6, C) amounts to hundreds of tons annually. In 1953 about 400 lb of B_{12}, valued at over 14 million dollars, was obtained from microöorganisms.

High Polymers

Plastics, Resins, Fibers, Rubber · One of the most interesting and important trends of modern chemistry has been the rapid growth in the production and use of synthetic rubber, plastics, resins, and fibers. The table below shows the growth of the plastics industry.

Among the many familiar products of this development are such articles as brush handles, steering wheels, telephone receivers, electrical plugs and switches, nylon fibers and bristles, and the greatly improved lacquers used on automobiles and refrigerators. Hundreds of articles in common use which were formerly made of wood, glass, or metals are now being made out of these synthetic products.

	YEAR	SYNTHETIC ORGANIC RESINS (lb)	CELLULOSE PLASTICS (lb)
UNITED STATES PRODUCTION OF RESINS AND PLASTICS	1927	13,452,000	—
	1933	45,200,000	15,825,000
	1937	163,031,000	37,047,000
	1940	276,814,000	35,765,000
	1943	653,938,000	68,000,000
	1946	1,025,118,000	121,000,000
	1949	1,491,111,000	—
	1952	2,190,000,000	98,000,000

Reasons for the Rapid Development of the Plastics Industry · There are many reasons for this development. Among these are:

1. **The ability to suit the product to the need.** Wood, rubber, silk, and other natural products must be used largely in the form in which they come from nature. For some purposes these products are satisfactory; for others, only partially so. The chemist can come very close to preparing a synthetic product with the *exact* properties desired, by suitable modification of the manufacturing procedure. His object is not merely to provide substitutes for natural materials but to improve on them.

2. **National self-sufficiency.** The importance of synthetic rubber is now well known to all. When access to the great rubber-producing areas of the Far East was cut off in 1940, an acute shortage of this critical material arose. American chemists undertook to make a rubberlike material, and within a few years were producing rubber of satisfactory quality and in large quantity. More synthetic rubber is now used than natural rubber. Products such as nylon are not only superior to silk in most respects but make this country independent of the silk-producing countries.

3. **Conservation of natural resources.** Supplies of wood, iron, and other natural structural materials are not unlimited. It is gratifying to know that chemists will often be able to make synthetic materials when the need becomes apparent, thereby reducing the consumption of these natural resources.

Fortunately it is possible to classify synthetic structural materials on the basis of their molecular structure and their methods of formation, and thereby to gain an insight into the reasons for the properties of strength, toughness, and durability that make them useful.

Molecular Nature of High Polymers · The natural and synthetic organic materials suitable for use as plastics, films, and fibers all have a very high molecular weight. This fact arises from their mode of formation from polyfunctional molecules (Chap. 30). Cellulose, the structural material of plants, has a molecular weight of 300,000 to 500,000. Proteins have molecular weights in the same range, while the molecular weights of nylon and cellulose acetate vary from 20,000 to 100,000. The molecular weight of Bakelite (phenol-formaldehyde plastic) is so high as to be indeterminable. Matter made up of these large molecules has properties different from matter made up of smaller molecules.

Chain and Cross-Linked Polymers · There are several ways in which the many high-polymeric materials may be classified. One convenient way is to separate them on the basis of their structures into *chain* and *cross-linked* polymers.

Chain polymers are those in which the large molecules are in the form of long chains. These chains may be straightened out, or they may be curled on themselves, but they are not chemically connected to each other. Polymers of this type are fiber-formers and rubbers. If the long chains are dissolved in a suitable solvent and the solution forced through a spinneret, with stretching, filaments are formed (Fig. 32-2). The solvent

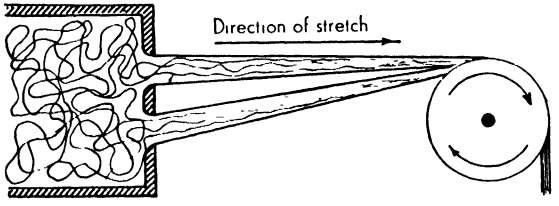
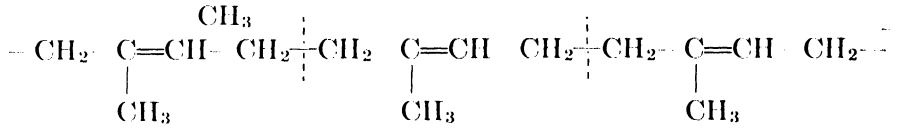


Fig. 32-2. Section of a Spinneret · Showing how the molecules of a high polymer are aligned to form a filament when the solution is stretched during drying or coagulation

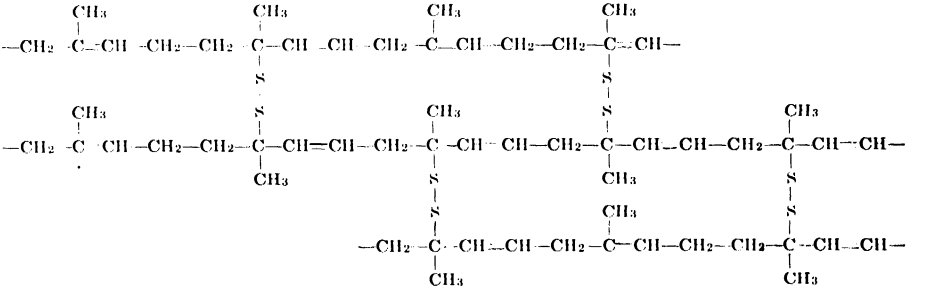
is evaporated (or the polymer precipitated) at the same time. The stretching tends to align the chains so that they lie closely enough together to let the van der Waals forces between molecules come into play,

which gives a strong thread when the filaments are spun. If the chains are made with bulky side groups attached, which tend to keep the individual chains apart, then the cohesive forces between chains are less pronounced, and the rubbery properties arising from the folding and coiling of the chains are obtained.

In cross-linked polymers the chains are connected together at various points so that a three-dimensional network is formed, and the long chains are further tied together to make a gigantic molecule big enough to see. Such molecules tend to be hard and insoluble, and to resist deformation. They make up the hard, molded plastics used for making toys and dishes. The effect of cross-linking may be readily observed by comparing soft, natural rubber with the hard rubber formed by vulcanizing natural rubber. Natural rubber is formed from repeated isoprene units ($CH_2-C(CH_3)=CH-CH_2-$) and has the structure



In vulcanization the rubber is heated with sulfur or sulfur compounds, and the chains are cross-linked through sulfur to give such structures as



The more sulfur we add, the greater is the proportion of cross-linking, and at 30% sulfur, the rubber becomes extremely hard and brittle.

Chain polymers soften on heating and hence are called *thermoplastic* polymers. They are easily molded by putting the warm material into a mold and allowing the mold to cool. A subsequent heating of the molded object will soften it again. Heavily cross-linked polymers do not soften on heating; they are called *thermosetting* polymers.

To mold these polymers the materials of which they are to be made are placed in a mold and then heated. The chemical reactions that lead

to cross-linking occur on heating the mold. After the reactions are complete further heating has little effect, until the temperature gets so high that actual chemical decomposition occurs.

Addition and Condensation Polymers · From a chemical standpoint polymers may be classed as *addition polymers*, in which the formula of the polymer molecule is some multiple of the formula of the polymerizing

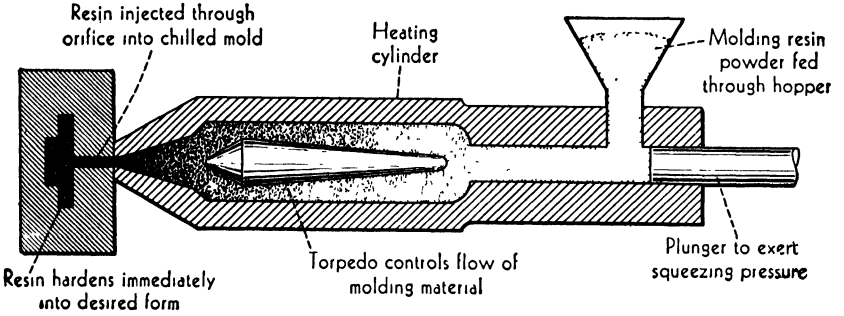
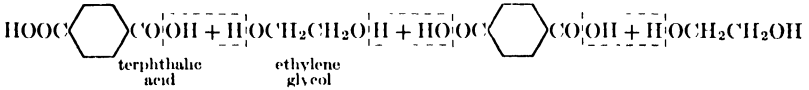


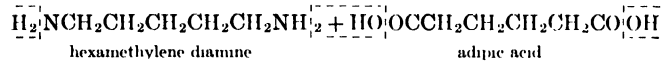
Fig. 32-3. A Cross Section of a Device for Molding Plastics by Pressure

molecule, and *condensation polymers*, in which each linkage formed between the polymerizing molecules results in the elimination of some small molecule, such as water.

The chemical reactions by which synthetic condensation polymers are formed are simply repeated steps of esterification or amide formation. Thus the synthetic fiber Dacron is formed by esterification,

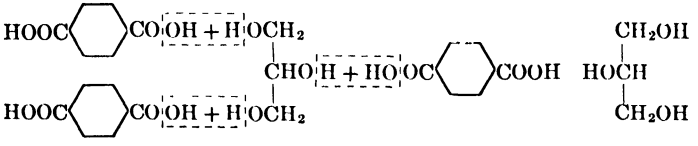


and nylon by amide formation:

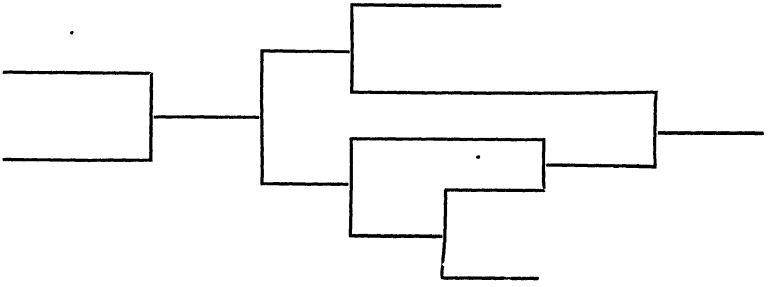


Note that in both cases the reacting groups are *bifunctional* ("containing two functional groups"), and that the molecules remaining after the indicated linkages have formed are still capable of further reaction with alcohol, acid, or amine groups on other molecules. Thus long chains or sheets can be built up from bifunctional molecules of this sort (Fig. 32-4).

If trifunctional molecules are added, then cross-linking, or branching, becomes possible, as in the alkyd resins, used in paints:



giving structures represented schematically as



where the vertical lines represent trifunctional units, and the horizontal lines represent chains built up from bifunctional materials.

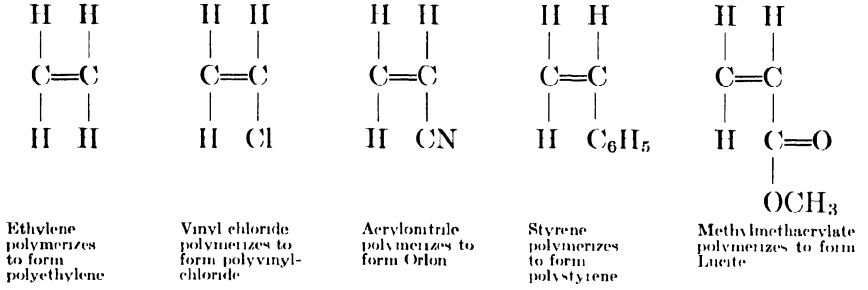


E. I. du Pont de Nemours & Co.

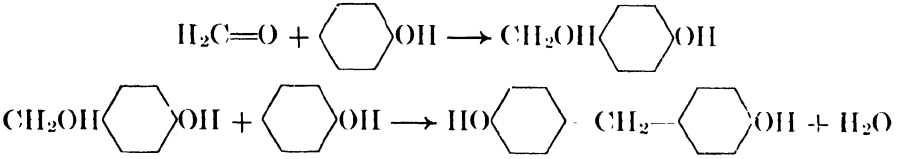
Fig. 32-4. The Strength of Mylar The sheet Mylar is chemically the same as the fibre Dacron, a condensation polymer (p. 578)

Addition polymers are those formed by self-addition at a double bond or at conjugated double bonds. Such a product has the same empirical formula as that of the monomer. Polymerized butadiene (p. 519) and polystyrene, as well as natural rubber, belong to this class.

Synthetic Plastics · Below are listed some of the more common starting materials (*monomers*) which will react, by self addition, to form chain polymers. Each of these monomers contains a double bond, which is reactive.

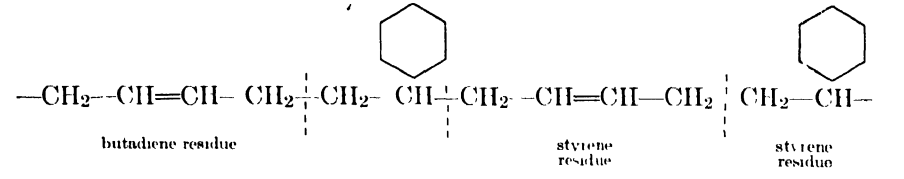


Formaldehyde Plastics · Some of the first plastics to be exploited commercially were those using formaldehyde. Bakelite is formed by a combination of addition and condensation between formaldehyde and phenol.



Further reactions of formaldehyde on the benzene ring in positions both ortho and para to the phenol group give rise to a highly cross-linked, hard resin, which is used to prepare many plastic objects. Resins of similar properties may be made from formaldehyde and urea.

Copolymers are made by allowing polymerization to occur between two kinds of double-bonded molecules. Thus good synthetic rubber is made by the copolymerization of butadiene and styrene, to give a molecule of the structure



The bulky styrene groups keep the chains apart and make the polymer more rubbery than polymerized butadiene alone. The polymer still contains double bonds, as does natural rubber, and it may be vulcanized.

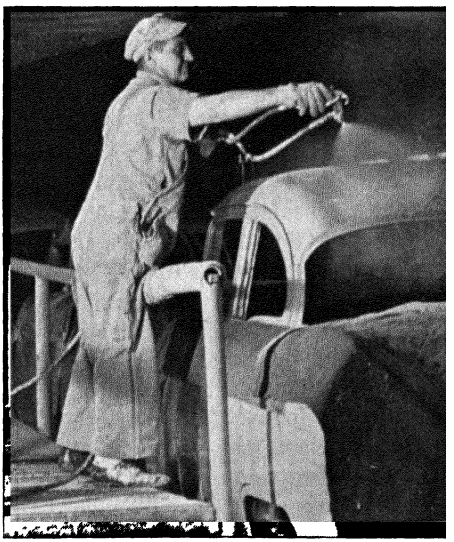
Paints, Varnishes, Lacquers

Remarkable progress has been made in recent years in the development and improvement of paints, varnishes, and lacquers. Much of this progress is the result of the use of synthetic organic compounds.

The Nature of Paints · A paint consists of two essential components: the vehicle and the pigment.

1. **The vehicle, or liquid medium.** The liquid portion of a paint consists of three components: (*a*) *Drying oils*, such as linseed oil, obtained from flaxseed, which will take up oxygen from the air and dry to a hornlike substance. (*b*) *Thinners*, consisting of turpentine or mineral spirits from petroleum, to reduce the viscosity to a suitable consistency for working. Such a thinner will evaporate after the paint has been applied. (*c*) *Driers*, or catalysts, to promote the drying. The inorganic compounds commonly used are oxides of manganese, lead, cobalt, or various borates, hydroxides, acetates, sulfates, carbonates, and chlorides.

2. **The pigment.** The pigment, or solid part of the paint, consists of finely divided materials chosen so as to give the desired surface and color. The pigment may be a white solid, such as white lead, zinc oxide, or lithopone. Titanium dioxide, either alone or mixed with other compounds, such as barium sulfate, calcium sulfate, and magnesium silicate, has come into wide use. The pigment also may be a colored compound, such as iron oxide (red), chromium oxide (green), Prussian blue, carbon black, or one of a wide variety of organic compounds.



General Motors Corporation

Fig. 32-5. Spraying an Automobile Body with Lacquer

The Nature of Varnishes · A varnish, like a paint, may be considered to be made up of a solid (nonvolatile) portion and a liquid medium.

1. **The solid portion.** Formerly the solid portion consisted exclusively of natural gums or resins obtained from certain trees, together with resinlike bodies, such as rosin, obtained from pine trees. At present the nonvolatile solids used are

largely synthetic gumlike substances. An important group of such substances are the alkyd resins (p. 578).

2. **The liquid portion.** In the usual type of varnish the nonvolatile solids, together with a drier, are dissolved in some appropriate oil, of which a score or more types are used. Prominent among these are dehydrated castor oil, soybean oil, fish oil, and tung oil.

The Nature of Lacquers · A lacquer is a special kind of varnish. Lacquers may be composed of (1) cellulose derivatives (known in the trade as "nitrocottons") or certain synthetic plastics; (2) a resin, including any of the synthetic varnish resins; (3) a plasticizer, such as castor oil and certain organic phosphates, to prevent cracking or breaking on drying; (4) a solvent, such as ethyl acetate or a similar ester; (5) a diluent, usually a coal-tar hydrocarbon or a similar petroleum distillate; and (6) a pigment color, either organic or mineral. The plasticizers, solvents, and diluents named above are simply examples. New ones are constantly coming into use.

QUESTIONS

1. Define (*a*) *polymer*; (*b*) *copolymerization*; (*c*) *cross-linked polymer*.

2. Distinguish between (*a*) cotton and mercerized cotton; (*b*) Dacron and nylon; (*c*) nylon and silk; (*d*) synthetic rubber and natural rubber; (*e*) Bakelite and Lucite; (*f*) vitamins and hormones; (*g*) paint and lacquer; (*h*) lacquer and varnish.

3. In general, what structural or functional groups should be present to promote polymerization?

4. What role do (*a*) the vitamins play in food metabolism? (*b*) the enzymes?

5. Suppose you wished to prepare a new drug or insecticide, what facts would be worth considering in planning your procedure?

6. Give two examples (*a*) of addition polymers; (*b*) of condensation polymers. (*c*) Write the equations for the polymerization reactions.

7. (*a*) What is an amino acid? (*b*) What is a protein? (*c*) Explain what happens to protein materials that are taken into the digestive system.

8. Write the equation for the formation of nylon.

9. What are the functions of (*a*) the proteins, (*b*) the fats, (*c*) the carbohydrates, as foods? (*d*) What other materials are necessary in a balanced diet?

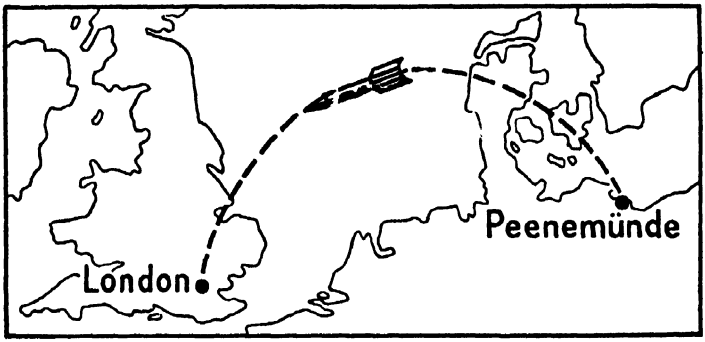
10. (*a*) Name the vitamins; (*b*) name the foods in which they are found; (*c*) tell the function of each vitamin in the body.

11. Why is ascorbic acid acidic?

12. Name the essential constituents of (*a*) paints, (*b*) lacquers, and (*c*) varnishes; and (*d*) explain their roles in the making of such protective coatings.

CHAPTER 33

FLAMES; JETS AND ROCKETS; EXPLOSIONS



Introduction · For many thousands of years man has known the art of making fire and of using glowing coals and flame as sources of heat. But only in very recent times are we beginning to learn something of the science of the burning process. Our efforts to learn more are stimulated by curiosity and by the desire to bring improvement to the performance of the flames in gasoline engines, Diesels, jets, and rockets.

We have learned, too, some of the fundamental facts about the behavior of explosives, including not only the venerable black powder known to the Chinese at least 2000 years ago, but also the whole family of versatile modern explosives. We seek better explosives and better control over those that we already possess, as we use their violent, disruptive power to serve our needs, both destructively and constructively, in war as well as in peace.

Flames

Combustion · The characteristic evidences of combustion are the evolution of heat and light (p. 54). The common combustion processes are those in which oxygen of the air reacts with a compound or compounds of carbon and hydrogen. The heat liberated in the complete combustion of natural gas (methane), according to the equation

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O\,(\textit{liquid})$$

is 212,800 calories for every mole (16 grams) of methane burned.

The Calorimeter · The heat of such a reaction as that above is measured in an instrument called a calorimeter. The reaction is made to take place inside a bomb or chamber immersed in water. The heat evolved in the reaction raises the temperature of the water; if the weight of water is known and the rise in temperature measured, the number of calories given off may be calculated. Corrections must be applied for the heat required to raise the temperature of the bomb containing the reactants, for the heat required to raise the temperature of the reaction products, and for any loss of heat to the surroundings.

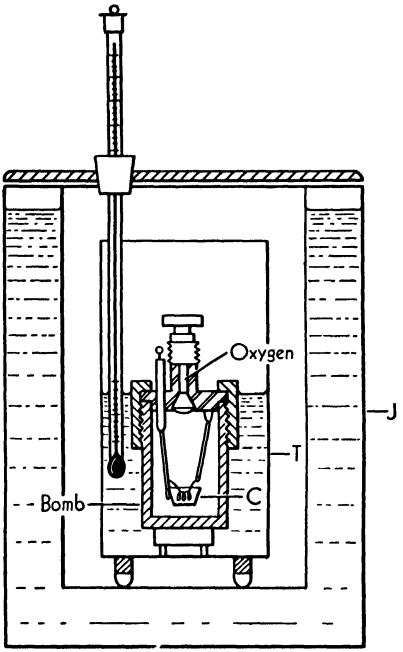


Fig. 33-1. Bomb Calorimeter The combustible substance, in small dish C, is fired by a hot wire and burns in oxygen admitted into the bomb. The heat is absorbed by the surrounding water in vessel T and the temperature rise measured by the thermometer. A jacket of water, J, surrounds the calorimeter

Visible Combustion · When combustion proceeds rapidly, the heat liberated is readily perceived, and the reaction is accompanied by light (p. 54). The products of combustion may be solids, as in the case of metals, such as iron; or they may be gases, as with carbon and sulfur. If the burning substance is a solid and remains so during combustion, it may become incandescent, but there is no flame. This is the case with the combustion of pure carbon and many of the metals. When both the substances involved in the combustion are gases, the bounding surface between the two presents the appearance known as a flame; and this flame is usually, though not always, distinctly luminous.

The fact that a flame often accompanies the combustion of solids (coal, wood, or a candle) or of liquids (oils) does not contradict the statements just made; for in such cases the heat of combustion produces vapors from the solid or liquid, and these in turn burn with a flame. If one end of a slender glass tube is held in the base of a candle flame, as indicated in

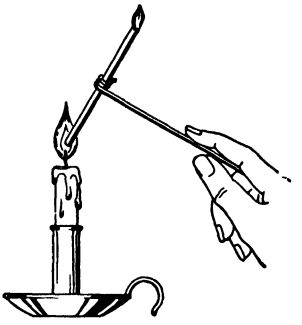


Fig. 33-2. Experiment to Show that the Solid Material of the Candle Vaporizes before Burning

Fig. 33-2, a flame is formed when a lighted match is held at the other end, showing that gases are produced from the candle which can be drawn off and ignited separately. The blue flame over a bed of coals is the flame of burning carbon monoxide formed by the partial combustion of the carbon (p. 490).

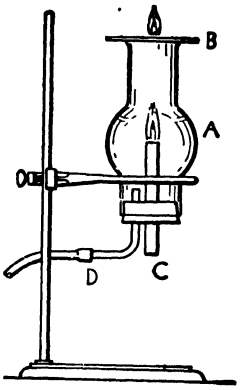


Fig. 33-3. Burning Gas in Air and Air in Gas

Relation between the Gases Forming a Flame · The gas issuing from a gas burner is said to *undergo* combustion, while the gas of the atmosphere about the flame is said to *support* combustion. This distinction is merely a matter of custom, since the relation of the two gases may be reversed without greatly altering the appearance of the flame.

Apparatus · Fig. 33-3 illustrates a convenient apparatus for demonstrating this fact. A wide-lamp chimney, *A*, is covered with a piece of asbestos board, *B*, which has a hole in the center about as large as a dime. A straight tube, *C*, about 1 cm in diameter, and also a smaller tube, *D*, connected with the gas supply, pass through a cork at the bottom. If the hole in *B* is closed (by a piece of asbestos board) while gas is admitted through *D*, the excess gas escapes downward through *C*, where it may be lighted. If the hole in *B* is now uncovered, at once the flame ascends to the top of the tube *C*. This flame is produced by air drawn up through *C*, burning in an atmosphere of fuel gas. Finally the excess of fuel gas may be ignited at *B*, where it will burn in air. We now have two flames, one produced by gas burning in air and the other by air burning in gas.

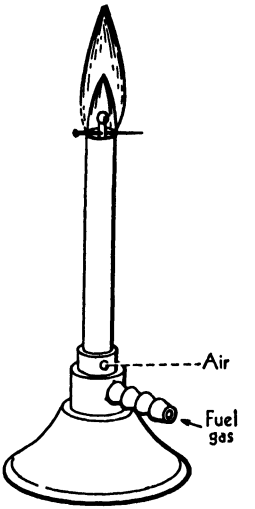


Fig 33-4. The Bunsen Burner · Showing a simple flame and the manner of premixing the fuel gas with air

Structure of a Flame · The flame of a Bunsen burner (Fig. 33-4) with its cylindrical chimney, or feed tube, is conical. The fuel gas is premixed with air; if it is methane, the best mixture will contain 1 volume of methane to 2 volumes of oxygen, or approximately 10 volumes of air. Such a mixture, however, is explosive (p. 593), and if it is ignited at the top of the burner the flame will "strike back" down the chimney. This does, indeed, happen when too much air is admitted to the mixture. In regular practice, the mixture is necessarily kept considerably short of sufficient air for

complete combustion; and though complete combustion of the fuel gas occurs within the boundaries of the flame, the rest of the oxygen needed is supplied by the air surrounding the outer mantle of the flame.

Simple Flames · When the chemical action taking place is that of hydrogen, carbon monoxide, or ethylene with oxygen, or of hydrogen with chlorine, the structure of the flame is very simple. It consists of two superimposed cones of different altitudes. The inner cone is composed of cool, uprushing, as yet unignited gas, and is therefore not a real part of the flame. A match head suspended in this region (Fig. 33-4) before lighting the gas is not ignited by the flame around it.

Complex Flames · In the burning of some hydrocarbons, as well as of many other gases, the flame is more complex, and as many as four distinct cones may be observed (Fig. 33-5). As we have seen, the innermost cone, *A*, is really not a part of the flame. If a Bunsen burner is employed, with the ring at the base turned to admit plenty of air, the second cone, *B*, is sharply defined and is bluish-green in color. As the air is shut off, it will be seen that a luminous spot appears at the apex of this cone, which gradually takes the form of a cone, *C*, quite covering cone *B* and brightly luminous over all its surface. Finally, if some object is held so as to intercept the light from this region, it will be seen that there is a fourth cone, *D*, which is only faintly luminous.



Fig. 33-5. A Complex Flame

Cause of the Cones · Since the gases which give rise to the multiplication of cones during combustion are always chemical compounds, such as hydrocarbons, it would appear probable that the cones are due to successive chemical reactions taking place in different regions. In the second cone (*B*) the original hydrocarbons burn to form carbon monoxide and hydrogen, together with some unsaturated hydrocarbons, chiefly acetylene and ethylene. In the third, or luminous, cone (*C*) the hydrogen and carbon monoxide are partly burned by the oxygen supply in the atmosphere, while the illuminants acetylene and ethylene are decomposed into carbon and hydrogen. The separated carbon becomes brilliantly incandescent and quickly undergoes combustion. The outer edge of the luminous flame marks its disappearance. The faint outside mantle (*D*) is the region in which the combustion of carbon monoxide and hydrogen is completed.

Conditions Affecting Luminosity · In general, anything that leads to an increase in the "cracking" of molecules or fragments of molecules that contain carbon, and so leads to an increase in the amount of sepa-

rated carbon in the flame, will tend to increase the intensity of the luminosity. Thus the nonluminous flame of a Bunsen burner becomes somewhat luminous when the tube of the burner is strongly heated; and an increase in concentration of the fuel gas leads to an increase in luminosity.

On the other hand, when the gas or the flame itself is cooled, the luminosity diminishes, as may be seen by bringing a large mass of cold metal, such as a flatiron, close to a luminous flame. Dilution with an indifferent gas, especially if it is cold, greatly reduces the rate of formation of free carbon, and so greatly reduces luminosity.

Some flames, such as that of burning ammonia, are luminous, though there is no solid incandescent product formed during combustion. It is possible that, in the decomposition into elements at a high temperature, endothermic compounds may give up some of their energy directly as light rather than as heat.

Flame Reactions · Recent research has shown that a very significant part of the flame is the thin mantle or flame front of the first cone, now known to be only about 0.02 mm thick, in which the combustion reactions are initiated and partially completed. The gas molecules of the mixture, rushing up from the Bunsen burner tube into the first or inner cone at a velocity of 100 to 200 ft per second, undergo partial reaction in the mantle, are heated by the heat of reaction and accelerated to velocities of the order of 3000 ft per second. They complete their flame reactions in about $\frac{1}{100,000}$th of a second.

These astonishingly fast gas-stream reactions of the Bunsen burner flame have been simulated in a "stovepipe" (Fig. 33-6) in such a way

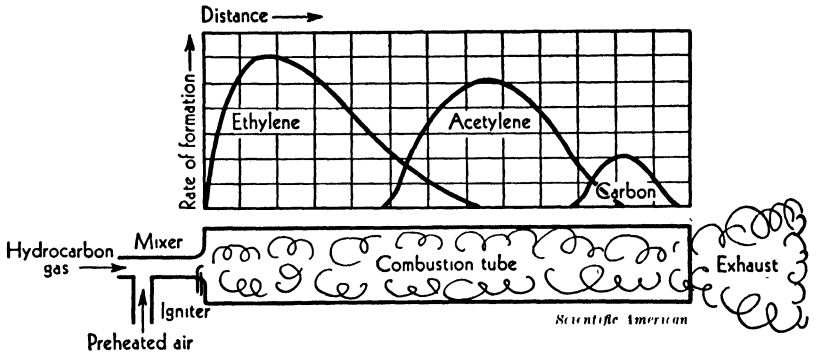


Fig. 33-6. A "Stovepipe" Combustion Tube

that the fuel gas and air reactants enter and the product molecules leave the pipe at substantially the same velocities as in the Bunsen flame, and

the reactions that occur are substantially the same as in the mantle or the inner cone; but here in the "stovepipe" they take place through a zone of several feet rather than only 0.02 mm.

When a mixture of hydrocarbon gases is burned in the pipe, the ethylene that forms first breaks down and re-forms into acetylene, which in turn cracks to form carbon. By cooling the pipe wall with water at the proper place, acetylene can be drawn off in quantity; and the general method promises to compete successfully in the commercial production of acetylene.

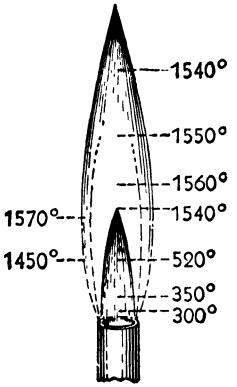


Fig. 33-7. Temperatures of Bunsen Flame

The Temperature of Flames · The actual temperature which can be realized in an ordinary flame obviously depends upon many conditions, such as the composition of the gas, its pressure, initial temperature, rate of flow, and the method of supplying the air. Even in an ordinary Bunsen flame, burning under favorable conditions, it is very difficult to determine the maximum temperature attained. The actual region of great heat is very limited, as the burning zones are very thin. The temperatures in different parts of the flame are very different, and any object placed in the flame to determine its temperature cuts across many different regions and is unequally heated. Under exceptional conditions it has been found possible to melt a very fine platinum wire in a good Bunsen flame, which shows that a temperature of 1755° is surely reached. The accompanying diagram (Fig. 33-7) gives a rough estimate of the probable temperatures in various parts of a good nonluminous Bunsen flame.

Reducing and Oxidizing Flames · Since the region just below the luminous cone is very hot and contains the reducing gases hydrogen and carbon monoxide, a substance such as a metallic oxide, placed in this region, will undergo reduction, provided it can be reduced by such hot gases. This region is therefore called the reducing region, and a body heated in this way is said to be heated in the *reducing flame*. There are no reducing gases at the apex of the flame, but it is very hot, and air is abundant; consequently a substance which is rather readily oxidized will undergo oxidation if heated in this region. This is called the *oxidizing flame*.

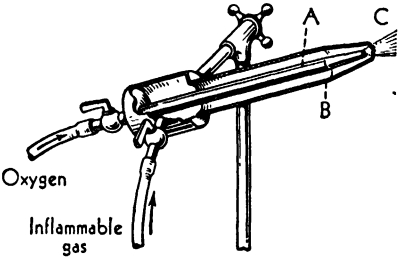
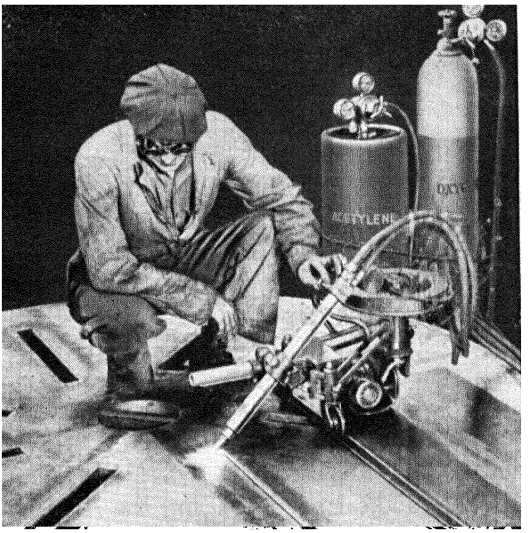


Fig. 33-8. Diagram of a Blowtorch

Blowtorch (Blast Lamp) · A blowtorch is a device for increasing the rate of burning in a flame, and hence the flame temperature, by feeding oxygen (or air) into the flame under pressure. The device consists of two tubes, *A* and *B*, one inside the other, as shown in Fig. 33-8. The inflammable gas is forced through the outer tube, oxygen through the inner, and the burning zone is concentrated at the tip, *C*.



Linde Air Products Company

Fig. 33-9. Showing the Use of an Oxyacetylene Torch to Cut through a Steel Plate

The first device of this sort was the oxyhydrogen blowtorch, invented by the American chemist Robert Hare (Fig. 33-10) in 1801. Burning hydrogen and oxygen, it reaches a temperature of 2000° C. The common welding torch (Fig. 33-9) uses acetylene and oxygen. In its flame the heat of decomposition of acetylene (exothermic reaction, p. 160) is added to the heats of combustion of the carbon and hydrogen, and temperatures of the order of 3000° C are produced. A torch burning powdered aluminum in oxygen produces 3500° C.



Fig. 33-10. Robert Hare (1781–1858) An early American chemist, born in Philadelphia, who invented the oxyhydrogen blowtorch. He specialized in the study of electricity, and invented numerous items of laboratory apparatus for testing and experimenting

A useful improvement of the oxyhydrogen torch is the atomic hydro-

gen torch, devised by Langmuir (Fig. 33-11). In it hydrogen is first passed through an electric arc, which causes it to dissociate into hydrogen atoms. The atoms pass out of the torch and recombine on contact with

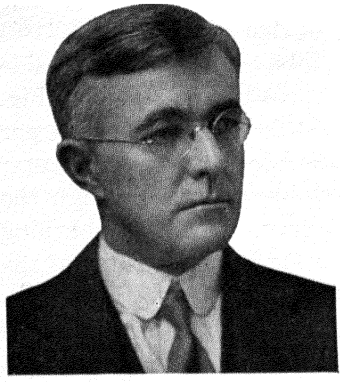


Fig. 33-11. Irving Langmuir (1881–). An eminent American chemist who has contributed much to our knowledge of atoms and molecules. In 1932 he was awarded the Nobel prize, generally regarded as the greatest honor that can come to any scientist.

the solid surface on which the torch is played, liberating the heat of formation of hydrogen molecules, 100 kcal per mole. To this is added the heat of combustion of hydrogen, 56 kcal per mole, and the resulting flame reaches temperatures of approximately 4000° C.

Jets

The principle of the operation of the jet engine is the same as that of the twirling lawn sprinkler and of Hero's engine (Fig. 33-12) of 200 B.C. "Reaction is equal and opposite to action." It is the "action," or the *thrust* of the fast-flowing stream of gas as it roars out of the exhaust nozzle in the rear, which in "reaction" drives forward the jet engine and whatever the engine is mounted on.

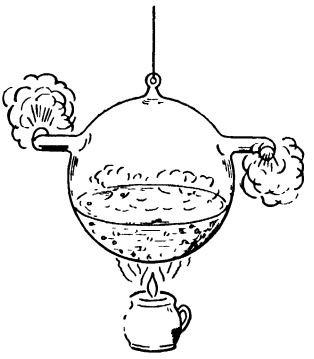


Fig. 33-12. Hero's Engine. The reaction from the jets of steam spins the boiler and its two arms.

Turbojet · One of the common types of jet engine is the axial-flow compressor, or *turbojet* (Fig. 33-13), invented and adapted for use in an airplane by the British engineer Whittle in 1930. This jet engine has three major parts. (1) a rotary compressor that takes in air, builds up its pressure, and delivers it to (2) the combustion chamber where the fuel is injected and burned, using part of the air, to form a continuous flame. Then the hot combustion gases and excess air rush on to the rear and out through

the exhaust nozzle at tremendous velocities. On their way they impinge on, and turn (3) the turbine, which drives the compressor. Both turbine and compressor are mounted on the same axle; and there is thus only one moving part.

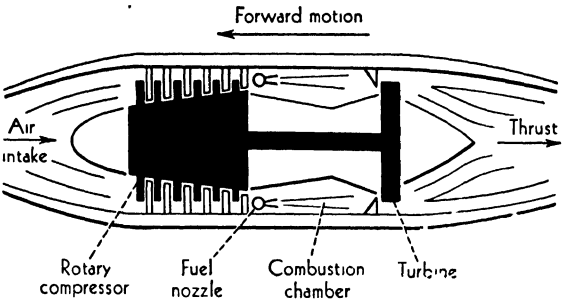


Fig. 33-13. Showing the Major Parts of a Turbojet

The turbojet engine, weight for weight, develops four times the horsepower of the piston engine. The top horsepower for the airplane piston engine is about 3,500, whereas some of the jet engines top 25,000 hp at supersonic speeds, and the B 52 jet bomber is said to develop more than 100,000 hp! Though the jet consumes fuel ravenously (about one pound of hydrocarbon fuel per hour per pound of thrust—and some engines have a thrust of 10,000 lb), a whole range of combustible materials may be used, which may soon include powdered coal.

A modification, designed to use more of the energy in spinning the turbine, makes a *gas turbine* suitable for use in stationary power plants. It is likely that this will in time displace the piston engine and steam turbine for such use, and it may be adapted also for automobiles and locomotives.

The Ramjet · The limiting factor in the use of the turbojet is that the material of which the turbine is made tends to soften, melt, and corrode at the high temperatures of the combustion gases. The *ramjet* eliminates the turbine and compressor by ramming the engine through the air fast enough to take in air and compress it. A modification of the ramjet in which

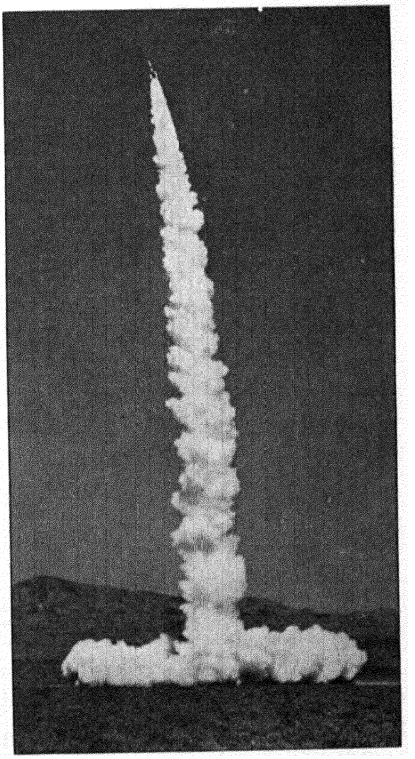


Fig. 33-14. Showing the Launching of a Rocket-Type Missile

air is taken in gulps through flapper valves whose operation is synchronized with explosions of the fuel mixture in the combustion chamber was used in the German V 1 rockets or "buzz bombs" in World War II.

The Rocket · The jet engines depend upon atmospheric air for their oxygen. Rockets, on the other hand, carry their own *oxidizer*, along

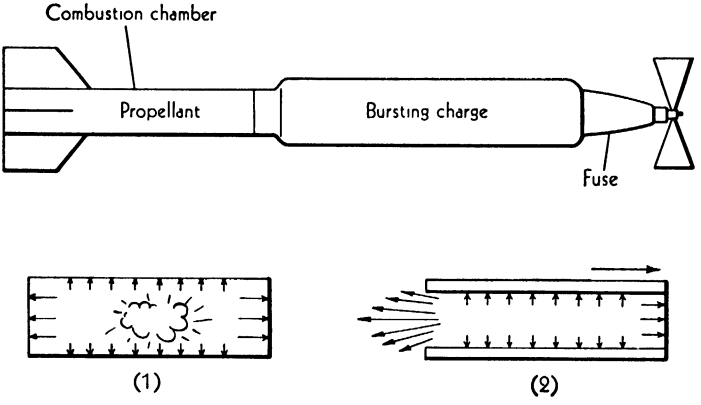


Fig. 33-15. A Military Rocket · A two-vaned mechanism driven by the wind arms a fuse in the head end so that explosion will occur when the rocket strikes the target

with a *fuel* (Fig. 33-15). This makes them independent of the earth-bound atmosphere, and also makes it possible to attain much higher temperatures, and hence higher pressures and greater thrust. Small rockets contain solid propellants such as guncotton, which require no additional oxidizer. Long-range rockets use liquid fuels such as alcohol, gasoline, aniline, or hydrazine, and liquid oxidizers, such as liquid oxygen, nitric acid, or hydrogen peroxide. These are mixed in the combustion chamber and react extremely rapidly, producing temperatures of 3000° C and higher, and extremely high pressures. If the combustion chamber were entirely closed, as at (1), (Fig. 33-15), the pressure would be exerted equally on the walls; actually the chamber has a hole at one end, as at (2). Here the gas has nothing to push against and rushes out as from a nozzle; but at the opposite end the pressure pushes the rocket forward.

Explosions

Explosions · An explosion is caused by a sudden change in the pressure of gases following chemical reaction, or by the sudden formation of gases from liquids or solids. The greater the pressure change, and the more rapidly it is produced, the more violent the explosion.

The explosion of a gas mixture is very much slower than the explosion

of a liquid, such as nitroglycerin, or a solid, such as TNT. In an engine cylinder the exothermic reaction between gasoline vapors and oxygen of the air starts at the spark plug and spreads in an accelerating wave front. The heat raises the temperature and pressure of the unburned gases ahead, and thus allows the activated hydrocarbon molecules and oxygen molecules to come more rapidly together. The piston is pushed back, and the "burn" probably requires about a hundredth (10^{-2}) of a second.

But in the case of nitroglycerin (p. 540), either as "liquid" or as "solid" —as in dynamite— the explosion is completed in a millionth (10^{-6}) of a second or even less. The reaction may be represented in a general way by the equation

$$4\ C_3H_5(ONO_2)_3 \longrightarrow 12\ CO_2 + 6\ N_2 + 10\ H_2O + O_2$$

The oxygen required for the reaction is already present in the molecules of the explosive itself; and the oxygen atoms originally attached to the nitrogen atoms are placed so close to the carbon and hydrogen atoms with which they are about to unite, either within individual nitroglycerin molecules or between closely packed neighbor molecules, that only a small shift in positions of the atoms is needed to allow a shifting of chemical bonds and conversion of reactants into products. Often the vibrations from a mechanical shock spreading through the substance will produce the shifts in positions. Then very hot gases are formed at tremendous pressure, in the original volume, and this gives them terrific bursting and disruptive force, as they move out from the center of the explosion.

Explosive Mixtures · Explosion of a gas mixture will not occur unless the mixture falls within certain limits of percentage composition. Thus if hydrogen and air are mixed, the resulting mixture is not explosive unless the volume percentage of hydrogen is above 9 per cent and below 65 per cent, at atmospheric pressure. In mixtures outside these limits the combination is so gradual, the heat is so largely absorbed by the excess gases present, and the pressure change takes place so slowly and is so small a fraction of the total pressure, that no explosion occurs. The following table gives both the lower and the upper limits of explosive

	GAS	VOLUME PERCENTAGE AT LOWER LIMIT	VOLUME PERCENTAGE AT UPPER LIMIT
EXPLOSIVE MIXTURES WITH AIR	Hydrogen (H_2)	9	65
	Methane (CH_4)	5	13
	Carbon monoxide (CO)	14	74
	Acetylene (C_2H_2)	3	73
	Water gas (essentially $H_2 + CO$)	12	66
	Coal gas (essentially $H_2 + CH_4$)	6	29

mixtures of several gases with air, expressed in volume percentages. The values are to be regarded as approximate, and hold for a gas pressure of 1 atm.

Mine Explosions; the Safety Lamp · Some of the disastrous mine explosions that we read about are due to the accumulation of methane in the air of the mine until an explosive mixture (*fire damp*) is formed. Fortunately, the ignition point of a mixture of methane and air is high, and its flame may be extinguished by cooling. In 1815 Sir Humphry Davy (p. 243) invented a miner's lamp, based on this principle, in which the usual chimney of a lantern is replaced by a wire gauze (Fig. 33-16). An explosion flame starting at the wick is so cooled by the metal wire that ignition ceases, and the explosion is confined to the interior of the lamp. The principle may be demonstrated by holding a wire gauze a few inches above a Bunsen burner, parallel to the table top (Fig. 33-17). When the gas is turned on and lighted *above* the gauze, the resulting flame rests upon the gauze but does not pass through it to the burner.

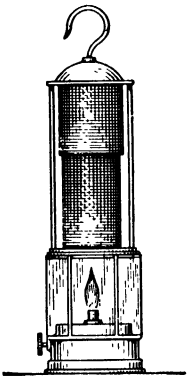


Fig. 33-16. Miner's Safety Lamp

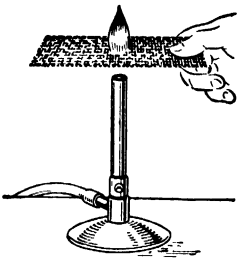


Fig. 33-17. Illustration of the Principle of the Miner's Lamp

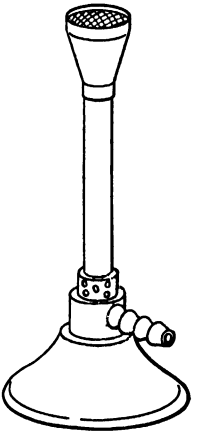


Fig. 33-18. A Meker Burner

Another illustration of the same principle is to be found in the *Meker burner* (Fig. 33-18). Here, enough air is mixed with the fuel gas, through the entrance holes at the bottom of the burner, to give an exeeedingly hot flame. But because of the cooling effect of the heavy wire gauze placed over the top of the burner, just under the flame, no "strike-back," occurs even though the uprushing gas has enough air in it to be an explosive mixture.

Dust Explosions · Some mine explosions, in fact most of those that occur in bituminous coal mines, are due to very finely divided particles of coal suspended in the air of the mine. The dust formed daily in the

operation of coal mines may amount to 3 to 5 per cent of the total coal production. Since 1902 there have been more than 350 major coal mine explosions, with a fatality list of the order of 10,000; and since 1860, when the first recorded dust explosion occurred in a flour mill in Milwaukee, about 1000 explosions caused by combustible dusts have occurred in industrial plants in this country, with an average of about one fatality for each explosion. Among the dangerous materials are metal dusts, such as magnesium and aluminum; cotton, wood, bark, and cork dusts; grain, starch, and sugar dusts, as well as plastics, sulfur, and some fertilizers in finely divided form.

Dust explosions resemble gas explosions, with flame fronts that accelerate, imparting heat to the regions of the dust cloud ahead. The smaller the size of a given quantity of dust particles, the larger is their total surface and area of contact with the air; and if the size is of colloidal dimensions (p. 466), the surface area can be enormous and the reaction with oxygen very fast and violent.

Internal-Combustion Engines · In the piston engines that are presently used in our automobiles and propeller-driven airplanes, the motive power

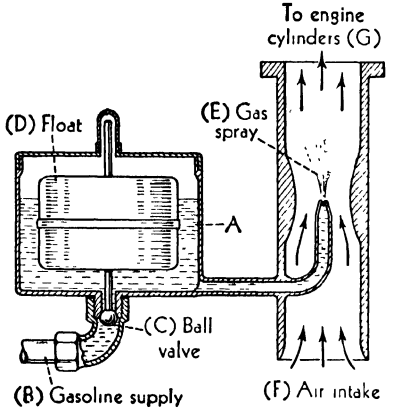
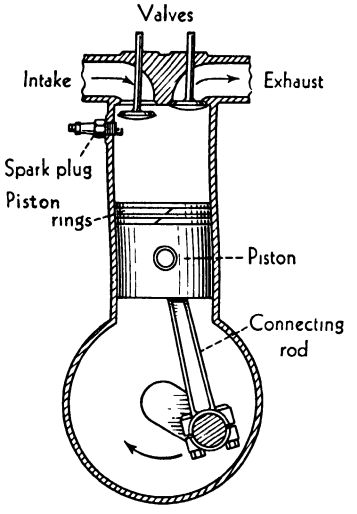


Fig. 33-19. Diagram Illustrating the Principle of an Automobile Carburetor · The gasoline enters the carburetor at *B* and is kept at a constant level in *A* by the float, *D*, and ball valve, *C*. The gasoline issues as a fine spray from the jet, *E*, and forms an explosive mixture with the air drawn in at *F*. This mixture passes through *G* to the cylinders of the engine, where it is exploded by a spark

comes from a mixture of gasoline vapor and air which is produced and controlled by the carburetor (Fig. 33-19), admitted to the cylinder and ignited by an electric spark (Fig. 33-20). The chemical reaction that takes place is a very slow explosion, as we have previously indicated, or perhaps merely a fast flame reaction, that gives a good push to the piston. However, under certain conditions the accelerating flame front may produce a detonation or "knock."

The efficiency with which we utilize the latent power of the gasoline fuel is disappointingly low. The most successful method so far developed



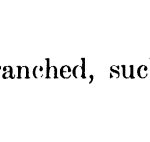
The operation of the ordinary automobile-engine cylinder is here shown. (1) The mixture of air and gasoline vapor from the carburetor is drawn through the *intake* on the downstroke of the piston (exhaust valve closed). (2) The upstroke of the piston compresses the gasoline-air mixture (both valves closed), and then the spark plug fires. (3) The impelling force of the rapidly expanding gases resulting from the explosion drives the piston down in the power stroke and through the connecting rod, and the crankshaft drives the flywheel. (4) The next upstroke pushes the gaseous products from the cylinder into the exhaust (intake valve closed). Then the engine is ready to repeat the cycle

Fig. 33-20. Gasoline-Engine Cylinder

for improving the efficiency involves increasing the "compression ratio" – which means the ratio of the volumes of the gasoline-air mixture in the cylinder before and after compression by the rising piston (Fig. 33-20). The greater the compression ratio, the greater the downward thrust of the piston. But also, unfortunately, the knock increases with the compression ratio; and it may become violent enough to damage the engine.

There are two ways of reducing or eliminating the objectionable knock.

1. Ordinary gasolines, composed largely of hydrocarbon molecules with their carbon atoms arranged in a straight chain (thus: C—C—C—C—C—), are prone to knock violently; but those made up of molecules which are more highly branched, such as



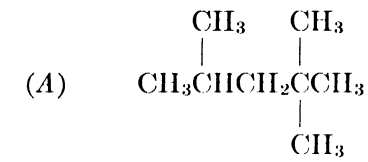
do not knock.

2. The knock can be prevented by adding to the gasoline a small percentage (1 to 3 ml/gal. of gasoline) of tetraethyl lead, $Pb(C_2H_5)_4$. Along with this there is added a small percentage of ethylene dichloride and ethylene dibromide (p. 270) or the very effective agent tricresyl phosphate, in order to form volatile compounds of lead which will be carried out through the exhaust. Otherwise lead and lead oxide would coat the spark plugs and other parts of the engine. A small addition of a

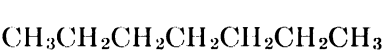
borane, $B[C(CH_3)_3]_3$, in so-called "boron gas," is said to keep carbon from forming in the engine and to have some anti-knock value.

Today the chemists and chemical engineers who design and make antiknock gasolines work together with the mechanical and automotive engineers who design and make engines, in an effort to improve fuel and engine performance. Through the two methods just mentioned, it has been possible during the period 1930 to 1954 to raise the average octane rating of premium gas from 74 to 92, and the average compression ratio from about 5 : 1 to 7.5 : 1, with the result that a 50-per-cent improvement in efficiency of use of gasoline has been achieved. If still higher compression ratios, perhaps even up to 12:1, can be reached, still further pickups in power returned for fuel consumed may be expected.

Antiknock Rating · In the standard method for rating the antiknock value of a gasoline, the branched isooctane (*A*) is arbitrarily assigned the value 100 per cent, while the straight-chain heptane (*B*) is called 0 per cent:



(*A*) octane (2, 2, 4-trimethylpentane)



(*B*) heptane

The former is very much better and the latter somewhat worse in antiknock properties than ordinary gasoline. By making the proper blend of these two and using it in an engine the intensity of knocking can be made to duplicate that of any gasoline to be tested. The percentage of octane isomer (*A*) in the blend required to equal the behavior of gasoline under test is called the *octane number* of the gasoline.

The Diesel Engine · None of our engines utilizes more than a small percentage of the energy in the fuel consumed. In the case of the ordinary steam engine the efficiency is less than 10 per cent. If we could find a way of utilizing all the energy in gasoline, 1 gallon of it would run our average automobile, traveling 30 miles an hour, 200 miles instead of the 15 to 20 actually covered. The modern Diesel engine, which is rapidly being developed and coming into wide use, is the most efficient type of engine; but even this does not utilize more than 40 per cent of the energy of the fuel consumed. In this type of engine, air is admitted to the cylinder of the engine and is highly compressed by the stroke of the piston. As a result of this compression, so much heat is generated that the temper-

ature reaches that of a red-hot stove. At the instant of greatest compression a fine spray of oil is forced into the cylinder. The temperature of the hot air is sufficient to ignite the mixture of oil and air, and the resulting explosion forces the piston down and so runs the engine.

Solid Explosives; Projectiles

Dynamite, Glyceryl Trinitrate (Nitroglycerin) · Dynamite is one of our most useful and versatile explosives. Its active ingredient, glyceryl trinitrate, generally though incorrectly called "nitroglycerin," may be made by allowing glycerin to react with nitric acid (p. 540):

$$C_3H_5(OH)_3 + 3\ HONO_2 \longrightarrow \underset{\text{glyceryl trinitrate}}{C_3H_5(ONO_2)_3} + 3\ H_2O$$

It is an oily liquid of slightly yellowish color; it is very explosive. It explodes by pressure or shock, by detonation, or by being heated to 250°. One volume of glyceryl trinitrate, on explosion, yields about 1300 volumes of gaseous compounds, which are expanded by the heat of decomposition to over 10,000 volumes. As we have already indicated, the enormous pressure that results from the sudden production of such a large amount of hot gases in a confined space is the cause of the shattering and disruptive effects of the blast.

Nitroglycerin is stabilized by being mixed with sawdust, wood flour, or other absorbent materials; and in this form it is called dynamite. The strength of the dynamite depends primarily on the percentage of glyceryl trinitrate present.

Dynamite is one of our most sinewy servants, literally able to move mountains. One pound of dynamite is good for blasting about 4 tons of materials that one may wish to loosen up or shake down from a solid bed or wall.

In 1953, industry in the United States set off about 757 million pounds of dynamite. The largest user was coal mining, with about 220 million pounds; second came quarrying, with 175 million; third, metal-ore mining, with 167 million; fourth, construction, with 115 million; fifth, seismographic prospecting, in which underground rock strata are shaken to determine whether they are of the type that might bear oil, 63 million pounds.

Historical. Nitroglycerin was first prepared by the Italian Sobrero, but it was not considered usable as an explosive because of its liquid state and poisonous qualities. In 1862 the young Swede Alfred Nobel (Fig. 33-21) determined

to manufacture this "blasting oil," though he had to place his factory on a barge and move it about as protests against its presence arose.

By a chance leak in a can of nitroglycerin he noticed that the infusorial earth in which the can had been packed had absorbed the liquid nitroglycerin to make a thick paste. He found this paste to be less readily explosive than liquid nitroglycerin and safer to handle. This was the first dynamite, patented in 1867.

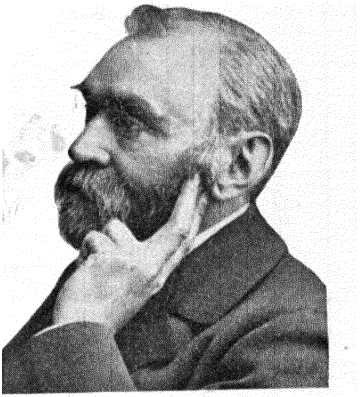


Fig. 33-21. Alfred Bernhard Nobel (1833–1896) · Distinguished Swedish inventor, and founder of the Nobel prizes

Nobel devoted his life to perfecting a number of high explosives, and died a wealthy man. He dedicated his fortune to the causes of universal peace and science. The Nobel Foundation, established in Stockholm in 1900, provides yearly awards of about $40,000 each to those five persons who, during the preceding year, have contributed most materially to human advancement in the fields of physics, chemistry, physiology and medicine, literature, and peace. At the discretion of the awarding committees in any given year, any of these prizes may be awarded jointly to two or more persons, or may be withheld entirely

Rifle Shells · The bullets that are shot from a .22 rifle are mounted in small brass shell cases that contain the propellant charge. This is usually black powder or smokeless powder (pp. 302, 546). The trigger actuates the hammer, and the hammer drives the firing pin against the base of the shell case at the rim, where, inside, there has been sprinkled a small amount of a *primer* Primers are sensitive to mechanical shock, will detonate under the hammer's impact and cause the powder to go off.

The sudden release of a large volume of hot gases, mostly CO, CO_2, and N_2, from the exploding black powder (p. 302) propels the bullet from the shell case and along the gun barrel with a "muzzle velocity" that ranges from 800 to 1200 ft per second, depending on the size of the propellant charge.

Artillery Shells · The much larger projectiles shot from cannon or big guns are also propelled from shell cases. The projectiles are made to be explosive. They are hollow, and for this reason are called *shells*; they are filled with an explosive which detonates when the shell approaches or strikes the target. The mechanism that causes the detonation is called the *fuse*, and it is mounted in the nose or in the base of the shell. To perform the complete act of firing the shell successfully requires the use of four different types of explosives: the propellant, the primer, the booster, and the bursting charge.

1. **The propellant.** The explosive in the shell case (Fig. 33-22) that drives the projectile out of the gun barrel must not explode too rapidly. Dynamite could not be used; it would blow the gun itself to pieces. A slow explosion, or even just a fast "burn," of the sort given by guncotton (cellulose nitrate, p. 545) is what is needed, though if glyceryl trinitrate is mixed with cellulose nitrate, a plastic mass is obtained which burns slowly enough and can be used as a propellant. The smokeless powders *Ballistite* and *cordite* are examples of double-base powders so called because they contain the two explosives nitroglycerin and cellulose nitrate.

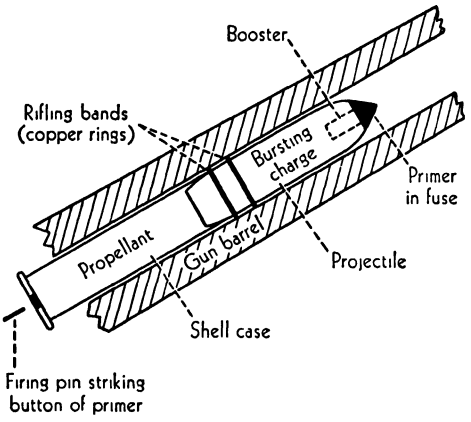


Fig. 33-22. An Artillery Shell

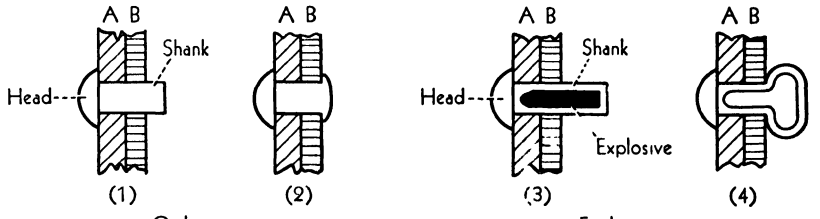
2. **The primer.** The primer is a relatively small bit of explosive, such as mercuric fulminate, $Hg(OCN)_2$, or lead azide, $Pb(N_3)_2$, very sensitive to mechanical shock. It is situated at the base of the shell case, and when struck by the firing pin ignites the propellant. Another portion of primer is in the fuse which is screwed into the nose of the shell and is detonated when the fuse hits the target, or when it is fired by some sort of timing mechanism.

The fuse, by itself or screwed into the nose of the shell (Fig. 33-22) is safe to handle before firing because it is *unarmed*. The fuse becomes armed when the shell moves up the barrel; the soft copper rings (see diagram) engage the spiral rifling inside the barrel and give the shell a spinning motion. Centrifugal force then operates a mechanism which arms the fuse.

3. **The booster.** Between the primer and the bursting charge in the shell is the *booster*. This is needed to help the primer and to ensure the explosion of the bursting charge, which is fairly inert and not easily detonated by the primer explosion alone. During World War I the booster was usually picric acid, $C_6H_2(NO_2)_3OH$; but more recently "tetryl," $C_6H_2(NO_2)_3N(NO_2)CH_3$, is used.

4. **The bursting charge.** The explosive in the shell must (1) be sufficiently difficult to set off so that it will not explode in the gun under the shock of the propellant's explosion, but (2) be readily induced to go off by the shock of the booster's explosion. TNT, trinitrotoluene,

$C_6H_2(NO_2)_3CH_3$, and amatol, a mixture of TNT and ammonium nitrate, NH_4NO_3, and also PETN, pentaerythritol tetranitrate, $C(CH_2NO_3)_4$, are commonly used in high-explosive shells.



In ordinary riveting practice, sheets or plates or other bodies may be fastened together by placing a malleable metallic rivet in position, as at (1), and pounding with a hammer on the end of the shank, while pressing on the head, until the shank has been beaten to form a solid clasp, as at (2)

The same result may be achieved in the case of small rivets with an explosion The rivet, which is hollow and filled with a heat-sensitive explosive of suitable violence, is in position, as at (3) The explosion may be set off by touching the head of the rivet with a hot soldering iron, for example. The explosion generates so high a pressure, and does it so rapidly, that ballooning of the metal shank outward is localized exactly where it is needed

Explosive rivets are widely used, particularly in situations where the shank end projects into a closed space—inaccessible to a hammer.

Fig. 33-23. Explosive Rivets

QUESTIONS

1. (*a*) How would you define a flame? (*b*) Why does water gas burn with a nonluminous flame? (*c*) Name two substances that burn without a flame.

2. In what units may each of the following quantities be measured: (*a*) heat of combustion; (*b*) temperature of a flame; (*c*) heating value of a fuel?

3. In stating the heat of combustion of hydrogen burning in oxygen, why is it necessary to specify whether the resulting water was a vapor or a liquid?

4. Would a miner's safety lamp with a chimney of woven glass or asbestos fibers be a success? Why?

5. Why do the windows of a room which is heated by an open gas heater so often "sweat" in cold weather?

6. Why should anthracite and coke be considered more desirable for domestic furnaces than soft coal?

7. By properly directing a flame on a piece of lead a chemist can change the lead to lead oxide and then change the lead oxide back to lead. In terms of the structure of the flame explain how these changes are brought about.

8. Write equations for the complete combustion (*a*) of *n*-pentane (C_5H_{12}); (*b*) of *n*-hexane (C_6H_{14}); (*c*) of *n*-octane (C_8H_{18}).

9. What is the difference between a flame and an explosion?

10. How is the antiknock value of a gasoline determined?

11. How does a blowtorch work? Is the oxyacetylene flame hotter than the oxyhydrogen flame?

12. Compare the method of making acetylene and ethylene in flame reactions with methods of preparation described in an earlier chapter.

13. What is the difference between a jet and a rocket?

14. Explain the function of the various types of explosives in the act of firing an artillery shell—the propellant, the primer, the booster, and the bursting charge (high explosive).

15. What is the principle of the miner's safety lamp? Can you give another illustration of the same principle?

PROBLEMS

1. The heat of combustion of 1 mole of *n*-hexane is 994.8 kcal, of 1 mole of *n*-heptane is 1150.8 kcal, and of 1 mole of *n*-octane is 1306.8 kcal. Estimate the heat of combustion of 1 mole of *n*-pentane.

2. (*a*) What volume of air, measured under standard conditions, would be required for the complete combustion of 1 gal of pure *n*-octane, of density 0 7036? (*b*) How much heat, measured in calories, would be liberated in the combustion?

3. A certain coal has a calorific value of 8000 cal/g. One ton of this coal will convert (*a*) what weight of water at 25° into steam at 100°; (*b*) what weight of ice at 0° to water at 25°?

4. If natural gas were pure methane, what weight of water would be formed in the combustion of 1 cubic meter of this gas measured at a temperature of 15° and a pressure of 750 mm?

5. In a room 15 ft × 12 ft × 10 ft there is a stove that burns 9 cu ft of natural gas per hour. The stopcock was accidentally turned on with the stove unlighted. Assuming that the gas was pure methane, calculate the approximate time that the gas must escape before an explosive mixture will be formed. (Assume that the amount of air in the room remains constant.)

6. A gas stove burning 6 cu ft of methane per hour is not connected with a chimney. (*a*) What weight of carbon dioxide will escape into the room if the stove burns for 7 hours? (*b*) What volume will this occupy at 20° and 750 mm pressure? (*c*) What weight of water vapor will be formed?

CHAPTER 34

ORES AND THEIR METALLURGY

General · One of the primary tasks of industry is the extraction and purification of useful substances from the materials of the earth's crust. Various elements, free or in compounds, are found there, sometimes widespread and sometimes concentrated in certain areas of the earth. The prospector locates these deposits, the chemist devises methods of extracting the useful product, and chemical and metallurgical engineers undertake the problems involved in putting these methods into practice.

Minerals and Ores · A few of the metals are often found free in nature and are then said to occur in the *native state.* Among these are gold, platinum, copper, bismuth, and in general those that stand low in the electrochemical series. Some of the nonmetals are also found in the free state, including sulfur (p. 371). As a rule, the metals and nonmetals are found *combined* in the form of oxides, sulfides, hydroxides, and salts of various acids. The most abundant of these salts are the silicates, carbonates, and sulfates All such natural substances as are essentially chemical individuals, whether they contain a metal or not, are called *minerals.* All minerals or mixtures of minerals which are of value for the extraction of useful substances are called *ores.*

Minerals and ores are a part of the wealth of any nation, and they are essential to the life of a great industrial nation. The uneven distribution of the essential ores and minerals causes many complex problems in international trade; it results also in a concentration of industry in certain parts of the world, and it has been one of the major causes of international disputes and, in fact, of wars. The major deposits of most of the minerals are controlled by a few nations.

Metallurgy · The science and art of extracting metals from their ores is called metallurgy. In general, it consists of (I) preliminary treatment, (II) reduction, and (III) refining. The preliminary treatment may require concentration of the ore to remove impurities, and roasting to convert the ore to a form more easily reduced.

I. ***Preliminary Treatment: Concentration and Roasting of the Ore*** · Most of the heavier metals, such as zinc, copper, lead, silver, and gold, are found either as sulfides or as native metals. The rich deposits of the world have become largely exhausted, and it is now necessary to use low-

grade ores often containing as little as 1 per cent of the desired metal. These ores must be crushed and the valuable portion *concentrated* before the metals can be obtained from them. The principal methods for concentrating the ores are the following:

1. **By washing.** This may be accomplished by stirring the crushed ore in running water. The worthless rock material, gangue, is lighter than the metal mineral and is largely washed away, leaving the heavier ore in concentrated form.

2. **By flotation.** An ingenious and effective method of concentration is called *flotation*. The finely crushed ore is churned up into a froth with water and a little oil often pine oil or cresylic acid. Although the particles of sulfides or of metals are much heavier than either water or the powdered rock, when coated with oil they stick to the bubbles of froth, and are *floated* off with the froth into settling-basins, from which a very concentrated ore is recovered for reduction (Fig. 34-1). Were it not for this flotation process, the heavy-metal industries could not work most of our mines on an economic basis.

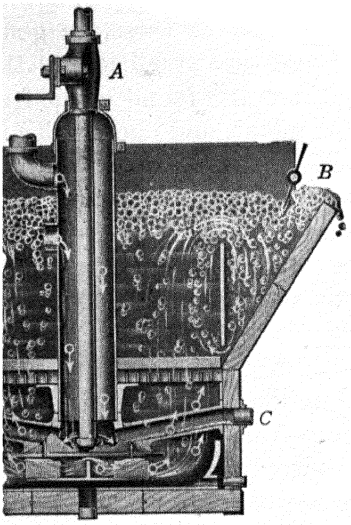


Fig. 34-1. The Flotation Process · Powdered ore, water, oil, and air are delivered into the shaft, *A*, and beaten to a froth by the fan at the base of the shaft. Air bubbles carrying the values in the ore rise as a froth and overflow at *B*. The worthless gangue sludges off at *C*.

In general, the process is limited, chiefly, to free metals or sulfide ores, and is most used with ores of copper, lead, and zinc. It is not, however, exclusively limited to such minerals. The process has been applied with marked success to the small particles of phosphate rock in Florida. Many millions of tons of ore of various metals are concentrated annually by flotation in the United States. In actual operation small quantities of frothing agents and stabilizers (about 1 oz to the ton) are added as may be needed to secure the best results.

3. **By the use of a magnetic field.** A few minerals are strongly magnetic. Advantage may be taken of this property to separate such minerals from a mixture.

4. **Roasting.** An ore is often subjected to a heating, or roasting, process before it is reduced. The purpose of this operation is to drive off water, carbon dioxide, or other volatile matter and to burn at least some of the sulfides into sulfur dioxide. The roasting of a sulfide ore converts the

ore into the oxide or a mixture of the oxide and the sulfide, which is then readily reduced to the metal.

II. ***Reduction*** · The main part of the metallurgical process (except where native ores are concerned) is the reduction of the ore to the free element (metal). Essentially this involves replacing the electrons lost by the metal atoms when they combined with the atoms of other elements to form ores. The reducing agent used in this process must fulfill at least two requirements: (1) it must be a sufficiently strong electron donor to force the metal ion to take up electrons, and (2) it must be cheap enough to make the process economically possible. The element that meets both these qualifications in many cases is carbon. Frequently it is found practical to use the electric current to bring about reduction; this usually depends upon the availability of cheap electric power.

1. **Reduction by electrolysis.** Metallic zinc may be deposited on the cathodes from a solution of zinc sulfate or other soluble zinc salt in water (p. 722); but metals that act rapidly on water, such as sodium or magnesium, are obtained by the electrolysis of *melted* salts. Some ores of copper or zinc are dissolved by acids, and the metal is obtained by the electrolysis of such solutions.

2. **Reduction of an oxide by carbon or carbon monoxide.** Many of the metals occur in nature in the form of oxides or in minerals that can be converted into oxides. When these oxides are heated with carbon, they are nearly all reduced, as illustrated in the equations

$$2\ CuO + C \longrightarrow 2\ Cu + CO_2\uparrow$$
$$Fe_2O_3 + 3\ C \longrightarrow 2\ Fe + 3\ CO\uparrow$$

The carbon is oxidized either to the dioxide or to the monoxide, according to the temperature which it is necessary to employ. High temperatures result in the formation of carbon monoxide, which may serve directly as the reducing agent, as is the case in the blast furnace (p. 609).

$$Fe_2O_3 + 3\ CO \longrightarrow 2\ Fe + 3\ CO_2$$

The chief difficulty with this method is that at very high temperatures many of the metals combine with excess of carbon to form *carbides*, so that the carbide rather than the free metal is obtained.

3. **Reduction of an oxide or a sulfide by aluminum.** When a very high temperature is required for carbon reduction, and the tendency of the metal to form a carbide is great, aluminum may sometimes be used as the reducing agent in place of carbon. For example, the element chromium may be prepared in this way:

$$Cr_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Cr$$

This method is known as the Goldschmidt method, since it was developed by a German chemist of that name.

Just as oxygen may be removed from an oxide by aluminum, so sulfur may sometimes be removed from a sulfide by aluminum or by iron. For example, antimony and lead are sometimes desulfurized by scrap iron:

$$Sb_2S_3 + 3\ Fe \longrightarrow 3\ FeS + 2\ Sb$$

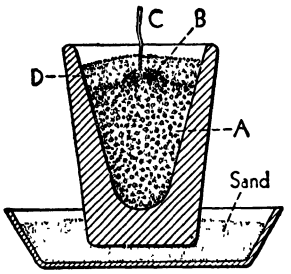


Fig. 34-2. Diagram Illustrating the Goldschmidt Method

Preparation of chromium by the Goldschmidt method. A mixture of chromium oxide and aluminum powder is placed in a clay crucible (*A*, Fig 34-2), and on top of it is placed a small heap, *B*, of a mixture of sodium peroxide and aluminum, into which is stuck a piece of magnesium ribbon, *C*. Powdered fluorspar, *D*, is placed around the sodium peroxide, after which the crucible is set on a pan of sand and the magnesium ribbon is ignited. When the flame reaches the sodium peroxide mixture, combustion of the aluminum begins with almost explosive violence, so that great care must be taken in the experiment. The heat of this combustion starts the reaction in the chromium oxide mixture, and the oxide is reduced to metallic chromium, which collects in the bottom of the crucible

III. ***Refining*** · After reduction it is usually necessary to subject the metal to a process which will remove the small amounts of other elements that are usually present. There are several ways of doing this, depending on the metal being purified. Copper is refined by an electrolytic method (p. 706), iron by the open-hearth furnace (p. 615), and mercury by nitric acid treatment followed by distillation (p. 727). Frequently the method of purification depends upon the degree of purity desired.

The Steps in the Metallurgy of Iron

One of the most important metallurgical processes is that by which iron and steel are prepared. Because of its great industrial importance and because the process illustrates many metallurgical principles, we propose to consider it here in some detail.

Occurrence · Iron has been in use as a metal for over four thousand years, since its ores are very abundant and it is not difficult to prepare the metal from them in fairly pure form. It occurs in large deposits as oxides, sulfides, and carbonates, and in smaller quantities in a great variety of minerals. Indeed, iron in small percentages is present in most rocks and soils, and it is assimilated by both plants and animals. It

processed in a blast furnace, and the resulting *pig iron* either is finally made into *cast iron* (and an extremely small fraction into *wrought iron*) or is further treated in *Bessemer converters*, or in *open-hearth* or *electric furnaces*, to make steel. The development of the huge modern furnaces and of the present great scale of production has demanded a remarkable application of engineering skill. Let us now trace the various stages of the metallurgical processes, from iron ore to final product.

Blast Furnaces in the United States · After being mined on the Mesabi Range, the various grades of the *hematite ore*, following some washing and "jigging" to concentrate the leaner ores, are blended to give a uniform stock containing 51.5 per cent iron; and this is shipped in lake boats, during the eight-month season, through Sault Sainte Marie to the various lake ports for delivery to blast furnaces. Most of our blast furnaces are located in a few states. In 1954 there were 78 in Pennsylvania, 53 in Ohio, 23 in Indiana, 22 in Illinois, 21 in Alabama, 17 in New York, 9 in Maryland, 7 in Michigan, 5 in West Virginia, and 5 in Utah; the rest of the total of 260 were scattered among eight other states. The total capacity of these furnaces was about 82,000,000 tons of pig iron.

The Metallurgy of the Blast Furnace · There are three primary functions of the blast furnace:

1. The first function is to reduce the ionic iron in the iron ore to metallic iron:

$$Fe^{+++} \longrightarrow Fe, \quad \text{or} \quad Fe^{++} \longrightarrow Fe$$

This is done by heating the ore with the reducing agents solid carbon (coke, coal, or charcoal) and carbon monoxide gas. The final iron obtained is called *pig iron*. At least 99 per cent of the pig iron throughout the world is made with coke. The coke is not only one of the reducing agents, but also the fuel which burns and generates the heat. The probable chemical reactions are, first, the formation of carbon dioxide and carbon monoxide near the bottom of the furnace,

$$C + O_2 \longrightarrow CO_2$$
$$CO_2 + C \longrightarrow 2\,CO$$

and, second, the partial reduction of the iron ore (say, hematite) by carbon monoxide,

$$Fe_2O_3 + CO \longrightarrow 2\,FeO + CO_2$$

followed by the complete reduction by the hot coke,

$$FeO + C \longrightarrow Fe + CO$$

2. The second function of the blast furnace is to dispose of the impurities of the ore and the ash from the coke. This is accomplished by adding a *flux* to the furnace charge to form a *slag* with the impurities.

Since silica is generally the predominant impurity in the ore, limestone ($CaCO_3$) is usually employed as the flux:

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$CaO + SiO_2 \longrightarrow CaSiO_3 \text{ (silicate)}$$

If oxides of less acidic character, like Al_2O_3, are present in the ore or ash, they also react with the lime and silica to form a fusible, glassy silicate slag.

3. The third function is to separate the metallic iron from the slag. The ore itself can be reduced at a temperature considerably below the melting point of iron. But the best way to separate the iron from the slag is to maintain a temperature hot enough to melt them both, at the bottom of the furnace, and allow them to separate automatically into two layers by virtue of their greatly different densities.

Details of the blast-furnace process. The modern blast furnace is usually about 100 ft high and about 27 ft in internal diameter at its widest part, narrowing somewhat toward both the top and the bottom (Fig. 34-4). The walls are built of steel and are lined with firebrick. The base is girdled with a pipe, *A*, *A*, through which a blast of hot air is forced. Leading from this are smaller pipes, *B*, *B*, called *tuyères*, which conduct the blast of hot air into the furnace. At the base of the furnace is a taphole, *K*, for the molten iron, through which the liquid metal can be drawn off from time to time by the conduit *C*. There is also a second opening, *L*, somewhat above the first, through which the excess of molten slag is drawn off by the conduit *D*. The top is closed by a movable trap, *G*, called the *double bell and hopper*, and through this the materials to be used are introduced. The gases resulting from the combustion of the fuel and the reduction of the ore, together with the nitrogen of the air admitted through the tuyères, escape through the pipe *E*. These gases have a temperature of about 300° and contain a sufficient percentage of carbon monoxide to render them combustible; they are accordingly utilized in large towers (stoves) set up alongside the furnace and often as large as the furnace itself, for heating the blast of air admitted through the tuyères. These gases are used also as fuel for internal-combustion engines which provide power for operating equipment in the steel mill.

For each ton of pig iron produced the charge to the furnace consists of about 2 tons of ore to 1 ton of coke to ½ ton of limestone, for common United States ores. (Such a charge requires the consumption of about 5 tons of air.) The charges are introduced at intervals into the furnace through the bell. At the bottom of the furnace the coke burns fiercely in the hot-air blast, forming carbon dioxide, which is at once reduced to carbon monoxide as it passes upward through the highly heated carbon.

The temperature of the furnace at the point at which the hot air enters is about 1600° C (about 2900° F), but it gradually decreases toward the top of the furnace, where it is about 300° C or 400° C.

is a constituent of hemoglobin, and plays a fundamental part in life processes.

World Iron-Ore Supplies · The principal iron-bearing minerals of the world, suitable as ores, are the following:

	MINERAL	FORMULA	IRON IN PURE MINERAL
IRON ORES	Hematite	Fe_2O_3	70.0 per cent
	Magnetite	Fe_3O_4	72.4 per cent
	Limonite	$x\ Fe_2O_3 \cdot y\ H_2O$	52.3 -66.3 per cent
	Siderite	$FeCO_3$	48.3 per cent

These minerals seldom occur pure in large quantities, but are found mixed with earthy substances, especially silica (and silicates), and often with sulfides and phosphates as well.

Many countries have iron-ore deposits, varying in quality from high-grade to good-grade: the United States (near Lake Superior and around Birmingham, Alabama), Brazil, England (in Cumberland and Lancaster), France (in Lorraine), Sweden, Chile, and Germany Also, Italy, Spain, India, Russia, Venezuela, and Canada (Labrador) have good deposits.

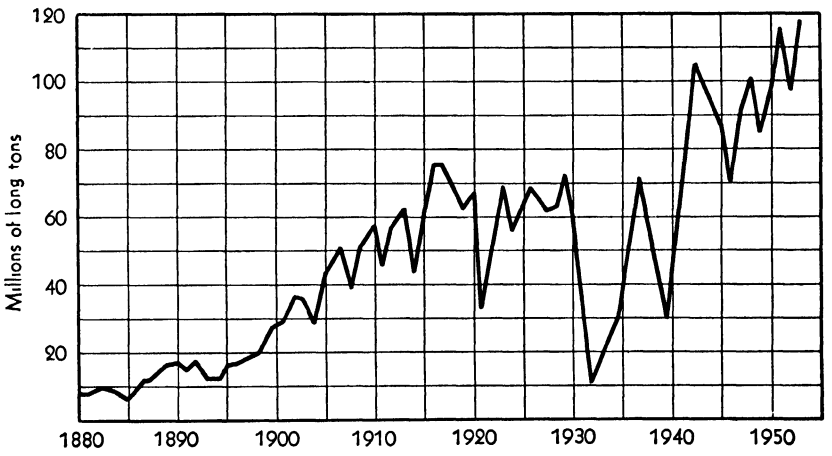


Fig. 34-3. Production of Iron Ore in the United States (1880–1953)

Production of Iron Ore · Production varies from year to year (Fig. 34-3). In 1953 nearly 120,000,000 tons of iron ore was mined in the United States, and in 1954 more than 132,000,000 tons, much of it in the great Mesabi Range in the Lake Superior region. In 1954 the European Community countries produced 66.8 million tons (France-Saar leading with 48.3 million tons and West Germany second with 10.7 million tons). In a normal year the very pure Swedish magnetic ore (about 70 per cent iron), which is used to make a fine-quality iron, is mined to

the extent of about 17,000,000 tons. Twenty-five countries each produce as much as 1,000,000 tons a year; but a small mine on the Mesabi Range will do as well. Although many of our important deposits are nearing exhaustion, new ones are being exploited, notably in Venezuela and in Labrador. It is possible that we might ultimately become dependent on the leaner-grade ores or on the *marginal ores* or on the so-called *formation materials* (silicate rocks carrying relatively small percentages of iron-bearing minerals).

Preparation of Pure Iron · Pure iron may be prepared in the form of a fine powder by heating the oxide in a current of hydrogen, though the product contains adsorbed hydrogen unless the process is carried out at a high temperature. It may be obtained in coherent masses by the electrolysis of ferrous sulfate solution between iron electrodes. To prevent the adsorption of hydrogen, which makes the metal hard and brittle, it is necessary to conduct the electrolysis at about 100°, to add some calcium chloride to the electrolyte, and to heat the product for some time in a vacuum. By such methods Burgess obtained iron said to be 99.98 per cent pure, and iron of nearly this quality can now be obtained commercially.

Properties of Pure Iron · Pure iron is a silvery metal having a density of 7.86 and a melting point of 1535°. It is ductile and malleable and is about as hard as an ordinary wire nail. It is especially well adapted to the manufacture of armatures and field pieces for dynamos and motors, since it acquires and loses magnetism much more rapidly than the ordinary varieties of iron.

The Iron of Commerce · Pure iron is rarely prepared and is of limited application, while iron which contains other elements exhibits a wide variety of properties and is of the greatest importance. Carbon is always present in quantities which range from mere traces up to 4.5 per cent. According to the conditions under which the metal is produced, this carbon may be in the form of graphite scattered through the iron, or as a solid solution of carbon in iron (if the iron is at high temperature), or in combination with the iron in the form of a carbide. The most important of these carbides has the formula Fe_3C and is a hard, brittle substance known as *cementite*. In addition, manganese and silicon, together with traces of phosphorus and sulfur, are usually present.

The properties of iron are greatly modified by the percentages of these and other constituents, by their form of combination in the iron, and by the treatment of the metal during its production from the ore. The varieties of iron recognized in commerce are *cast iron*, *wrought iron*, and *steel*.

The Metallurgy of Iron · The problem to be solved in the production of iron is (1) to obtain the metal, and (2) to produce it on a very large scale. Attention must be given to the removal of the rocky material, or gangue, in the ore, which is never a pure oxide. The iron ore is first

It cannot be welded or forged, although it can now be made malleable by a special treatment which converts all the cementite into graphite. It is rigid but not elastic, and its tensile strength is small. It is used for making castings which require no great strength, such as those for stoves, radiators, bases for machinery, and engine blocks. Cast iron, especially grades of high silicon content, is not acted upon by acids to the same extent as the purer grades of iron and so is used in making vessels for concentrating acids and for similar purposes.

Wrought Iron · An old process for radically improving pig iron was to convert it into *wrought iron* by using iron oxide, in the presence of a flux, to burn out most of the carbon, silicon, phosphorus, and sulfur from the pig iron, in furnaces known as *puddling furnaces*. As the iron is freed from other elements, it becomes pasty, owing to the higher melting point of the purer iron, and in this condition forms small lumps, which are raked together into a large one stuck together by the viscous slag. The large lump is then removed from the furnace and rolled or hammered into bars, with most of the slag squeezed out in this process.

A much more rapid process (the Aston process) is displacing the puddling furnace. This consists in pouring a pure grade of iron (known as Bessemer iron) into a prepared, melted slag and mixing the two together. This material is cast into ingot molds and is then rolled and hammered until the excess slag is squeezed out. The resulting iron has exactly the same physical structure as that made in the puddling furnace. Wrought iron has a fibrous structure, for it is composed of elongated grains of pure iron (*ferrite*) interspersed with elongated granules of slag. The ferrite present contains less than 0.3 per cent of carbon and small amounts of other elements. Wrought iron is soft, malleable, and ductile. While its tensile strength is greater than that of cast iron, it is less than that of most steel. Its melting point is much higher than that of cast iron. Wrought iron is no longer produced to the same relative extent as in former years, but its *actual* production tends to increase somewhat, owing to its usefulness where resistance to rust and corrosion is important.

Steel

Steel is iron containing carbon, in the range of 0.1 to 1.5 per cent, with or without the addition of other alloying elements. Like wrought iron, it is made from pig iron by first burning out a part of the carbon, silicon, phosphorus, and sulfur; however, the processes used are very different and the scale of production is vastly different. The total production of steel in the United States in 1953 was 111,609,000 tons, of which 90 per cent was made by the basic open-hearth processes, 5 per cent by the Bessemer process, and about 4 per cent in electric furnaces.

Acid Bessemer Process · In the acid Bessemer process the furnaces used are lined with siliceous materials, including *silica*, which, it will be recalled (pp. 53, 498), is an *acid anhydride*. These furnaces remove from the pig iron the carbon, manganese, and silicon, but the acid lining could not withstand the *basic* slag that would be needed to remove phosphorus and sulfur. The process is therefore employed when the pig iron used is, like some American pig iron, low in phosphorus and sulfur.

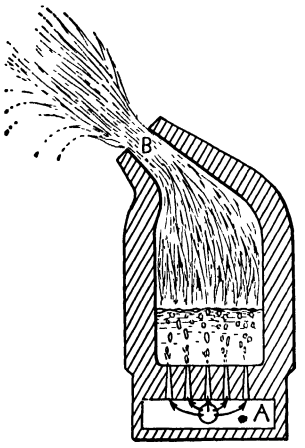


Fig. 34-6. Vertical Section Showing Details of a Bessemer Converter

Details of operation of the Bessemer process · This process, which was invented in 1855 by Bessemer and which gave the world its first low-priced steel, is carried out in great egg-shaped crucibles called *converters* (Fig. 34-6), each one of which will hold as much as 25 tons of steel. The converter is built of steel and lined with silica. It is mounted on trunnions, so that it can be tipped over on its side for filling and emptying. One of the trunnions is hollow, and a pipe connects it with an air chamber, *A*, which forms a false bottom to the converter. The true bottom is perforated, so that air can be forced in by an air blast admitted through the trunnion and the air chamber.

White-hot liquid pig iron from a blast furnace is run into the converter through its open, necklike top, *B*, with the converter tipped on its side to receive it; the air blast is then turned on, and the converter is rotated to a nearly vertical position. The carbon is probably oxidized directly by oxygen. The manganese and silicon in the iron are oxidized also (first the silicon and then the manganese), but not directly by oxygen. Some of the iron is oxidized,

$$2\ Fe + O_2 \longrightarrow 2\ FeO$$

and then this dissolved iron oxide reacts with the other elements:

$$Si + 2\ FeO \longrightarrow 2\ Fe + SiO_2$$
$$Mn + FeO \longrightarrow Fe + MnO$$

The acid silicon dioxide and the basic ferrous oxide and manganese dioxide together form a slag which consists largely of ferrous silicate ($FeO \cdot SiO_2$) and manganous silicate ($MnO \cdot SiO_2$).

The oxidation is attended by a brilliant flame. The heat of the reaction, largely due to the combustion of silicon, keeps the iron in a liquid condition. If the charge becomes too cold, more silicon, in the form of an iron-silicon alloy, may be added; if it gets too hot, it may be cooled down by throwing in cold scrap iron. The air blast is continued until the character of the flame shows that all the carbon has been burned away. The process requires on the average about ten minutes; and when it is complete, the desired quantity of carbon (generally in the form of high-carbon iron alloy or anthracite) is added and allowed to mix thoroughly with the fluid. The converter is then tilted and the steel run into

The reduction of the ore begins at the top of the furnace through the action of the carbon monoxide. As the ore slowly descends, the reduction is completed by the coke, and the resulting iron melts and collects as a liquid in the bottom

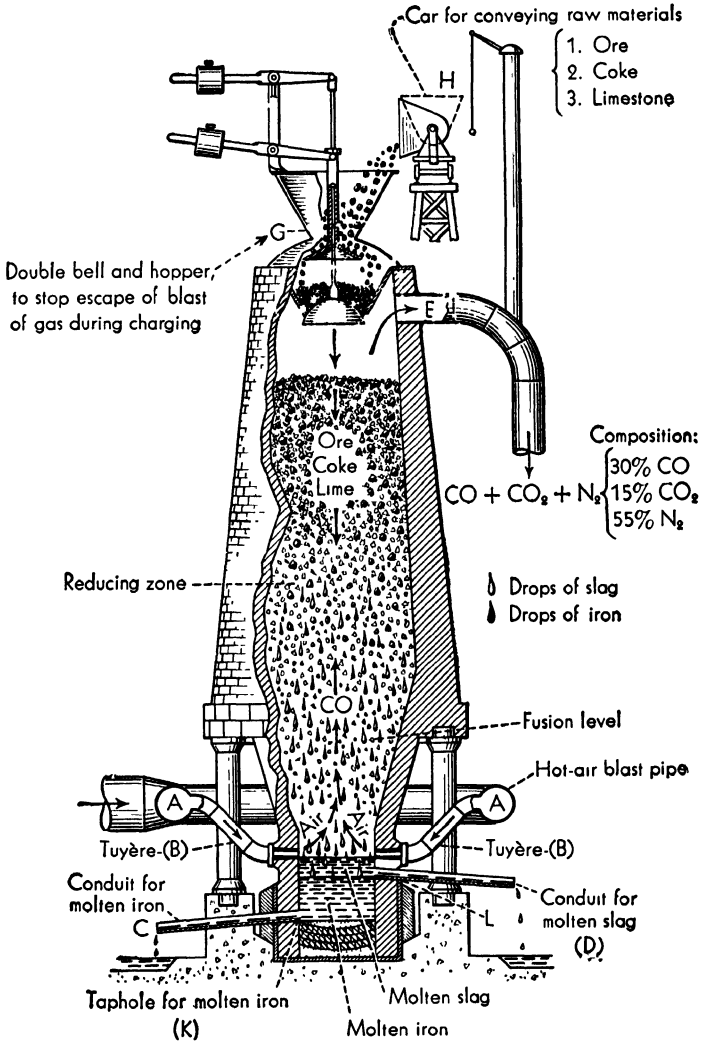


Fig. 34-4. Vertical Section of a Typical Blast Furnace

of the furnace, the lighter slag floating on top of it. After a considerable quantity of iron has collected, the slag is drawn off, and the iron is run out into large buckets and taken to the converters for the manufacture of steel; or it is run into iron troughs or molds lined with lime and connected in the form of an endless chain and cast as "pigs." The process of producing pig iron is a continuous one;

when the furnace is once started, it is kept in operation for months without interruption, or until the furnace requires repairing. The iron is withdrawn at intervals of about six hours, and often the production runs to 1000 tons or more in twenty-four hours.

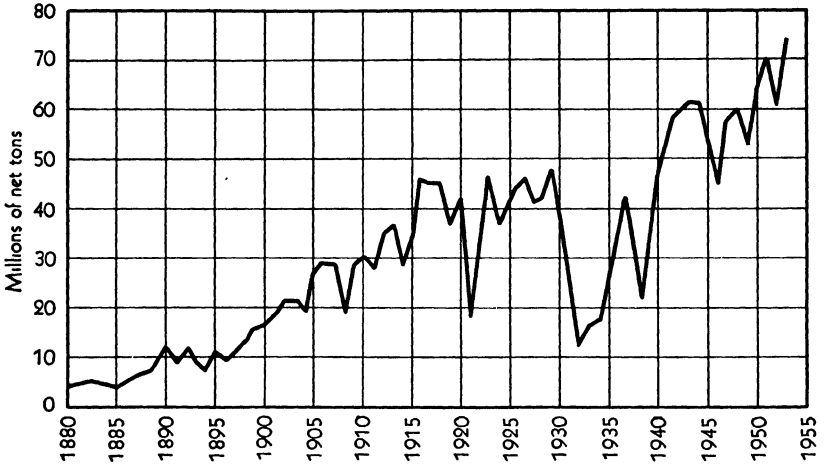


Fig. 34-5. Trend in the Production of Pig Iron in the United States (1880–1953)

Pig Iron · As it comes from the blast furnace, pig iron is the intermediate raw material from which all other varieties of iron are made. Because of excessive impurities and because the rate of cooling cannot be well controlled, it is weak and brittle and not fit for any other than very crude uses until refined. A fairly representative analysis (expressed in percentages) is as follows: C, 4.4; Si, 2.00; Mn, 0.80; P, 0.15; S, 0.04. The amount of pig iron produced in the United States is shown in Fig. 34-5.

Cast Iron · Cast iron is made from pig iron by a very simple process. A charge of pig iron, together with scrap iron of better quality (and sometimes other materials), is melted in a small furnace called a *cupola* furnace. The liquid metal is cast in sand molds, and the rate of cooling is carefully controlled, since this has much to do with the state of the carbon in the finished casting.

Cast iron varies considerably in composition but always contains over 2 per cent of carbon, variable quantities of manganese and silicon, and at least traces of phosphorus and sulfur. Two extreme varieties of cast iron are recognized: *gray* iron and *white* iron. In gray iron (slow cooling) the carbon is present partly in the form of *cementite* (Fe_3C) and partly as *graphite*, which gives the metal its gray color. In white cast iron (rapid cooling) almost all the carbon is in the combined state in the form of cementite. White cast iron is hard and brittle and melts at about 1100° C.

Mill Operations · When the steel ingot, whether rimmed or killed, has completely solidified, it is stripped out of the mold and heated for some time to a bright-red heat in a *soaking pit* (generally fired by gas) to relieve any strains that may have developed during the solidification process. The hot, plastic ingot then passes to the rolling mill, where it is worked down into various shapes by stepwise passes through steel rollers; or it may be drawn or sawed or forged. An idea of the relative amounts of the various general forms into which steel is fashioned in the United States is given by Fig. 34-8.

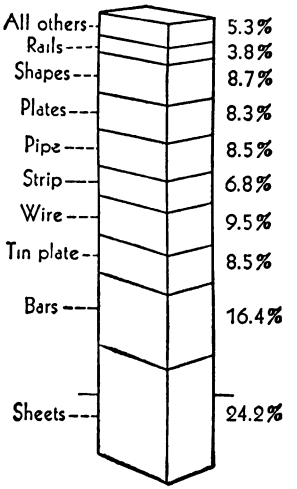


Fig. 34-8. Diagram Showing Percentage of Fashioned-Steel Products

Electric-Furnace Steel · A considerable quantity of high-grade alloy steel is made today in electric furnaces, generally of the arc type, in which the heat is generated in an arc that jumps between very large vertically placed graphite electrodes and the slag over the molten metal. There are many 75-ton electric furnaces in use. The capacity of such a furnace is much smaller than that of the open hearth, and therefore the control of the reactions is somewhat closer. Otherwise the principles involved in the steelmaking are the same.

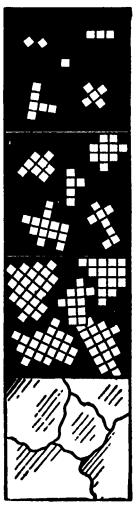


Fig. 34-9. Diagram Showing the Growth of Crystal Grains

Growth of Crystalline Grains · When steel solidifies in an ingot, crystals of the metal are formed. These crystals start at nuclei, little clusters of atoms, and grow out in all directions by adding on atoms, until neighboring crystal grains meet, as shown in Fig. 34-9, in the successive stages 1, 2, 3. The lines in 4 indicate the grain boundaries. (Compare with the photomicrographs of Fig. 34-10, p. 620.)

Into the grain boundaries are pushed many trace materials which are soluble in molten steel but not in the crystal grains. For instance, iron sulfide (FeS) collects at the grain boundaries; and since it is *melted* at the temperature of rolling and forging, its presence as a liquid film causes the steel to crack and break up along the grain boundaries. This may be prevented by the addition of manganese in sufficient quantity before pouring. Manganese sulfide (MnS) is formed; and while this too is trapped in the grain boundaries, it is a solid which does not melt at the temperature of hot-working the steel. For

this reason manganese is today regarded as an essential constituent of most steels.

Allotropy of Iron · Like many other elements, iron has allotropic forms. (1) Alpha iron, or *ferrite*: iron at ordinary temperatures is made up of grains which are crystals having a body-centered lattice (Fig. 35-1, A, p. 623). (2) Gamma iron, or *austenite*: above 910° the lattice changes to a face-centered form (Fig. 11-29, p. 188). (3) Delta iron: above 1390° (near the melting point of iron, 1535°) the lattice changes back to a high-temperature body-centered form.

The Tempering and Hardening of Steel · When steel containing from 0.5 to 1.5 per cent of carbon is heated to a temperature above 910° and then cooled suddenly by plunging it into cold water or oil, it becomes very hard and brittle. When reheated to temperatures ranging from 220° to 320° and then slowly cooled, this hard steel becomes softer and less brittle, and the process is called *tempering*. All such articles as springs and cutting tools are tempered in this way, each at a temperature best suited to its use.

Soft steel is sometimes hardened merely on the surface by a process called *casehardening*. The object is heated in powdered carbon or in various materials that yield carbon. The carbon slowly dissolves in the steel and converts the surface layer into high-carbon steel.

The carbon is present as cementite (Fe_3C), and hardening and tempering are explained in terms of what happens to the cementite. This is completely soluble in austenite (gamma iron), but *is not soluble* in ferrite (alpha iron). If, however, the hot austenite is transformed suddenly into ferrite by a quick chill, the cementite does not have time to crystallize out and is held in supersaturated solution in the ferrite. Ordinarily ferrite is relatively soft and plastic. But the "stranger" Fe_3C molecules intrude themselves between the layers of the ferrite lattice, dipping partly into one layer and partly into another, and "key" the layers together and prevent easy slippage of one layer over another. In this way the plasticity of the lattice is cut down, and the steel becomes brittle and extremely hard. Steel in this form is called *martensite*.

When the martensite is tempered by heating, the cementite precipitates out of the ferrite and builds little crystals of its own, thus leaving zones of soft ferrite in between the cementite crystals.

Alloy Steels · Of all the alloying elements, carbon is the most influential in steel. By variation of the carbon content of steel and by suitable heat treatment, a remarkably wide range of properties (ductility, malleability, strength, toughness, hardness) is available. Often we may wish to have a steel which is very hard, but at the same time tough rather

molds, and the ingots so formed are hammered or rolled into rails or other objects. The process must be conducted very rapidly, for as soon as the silicon and carbon have been burned, the iron will begin to burn up; moreover, since there is then no way to keep the iron from cooling, it must be poured at once.

Bessemer steel is suited to many standard articles, such as structural materials. It is sometimes cheaper than open-hearth steel, but is not adapted to such a variety of purposes.

Basic Open-Hearth Process · In the basic open-hearth process the hearth of the furnace is made of dead-burned magnesite (magnesia) or of clinkered dolomite, both of which act as *bases*. (The roof and walls of the furnace are usually made of silica brick.) In such furnaces most of the phosphorus and sulfur are removed, as well as the silicon and carbon. Since the presence of more than traces of phosphorus and sulfur in the finished steel renders the metal so brittle that it is worthless for most purposes, the open-hearth process possesses a great advantage over the acid Bessemer process in that it makes possible the utilization of iron ores (or pig iron obtained from them) that contain appreciable quantities of phosphorus and sulfur. The operation does not need to be hastened, and steel of any desired composition can be produced.

Details of the open-hearth process. Fig. 34-7 shows the simpler parts of the type of furnace used in this process. Open-hearth furnaces have capacities varying from about 50 to 500 tons of steel per melt, and two or three melts can be made daily. The hearth of a medium-sized furnace is about 40 ft in length, 12 ft in width, and 2 ft in depth, and is lined with magnesium oxide (calcined magnesium carbonate) (*A*, *A*). Either gas or sprayed oil or finely powdered coal is used as fuel. Below the furnace is placed a checkerwork of brick so arranged that the hot products of combustion escaping from the furnace may be conducted through it, thus heating the bricks to a high temperature. Both the air necessary for combustion and the gaseous fuel (unless decomposed by heating, as in the case of natural gas and sprayed oil) are preheated by passing them over the hot bricks, so that the temperature reached during combustion is greatly increased. The gas entering through *C* comes in contact at *D* with the hot air entering through *B*, and a vigorous combustion results. The flame passes over the charge in the furnace; and at regular intervals the direction from which the fuel and air enter the furnace is reversed.

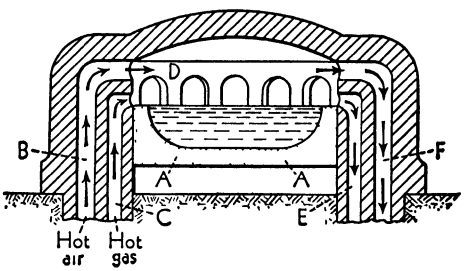


Fig. 34-7. Cross Section of an Open-Hearth Furnace

Charging the open hearth and melting down. Into the open hearth are charged limestone, steel scrap, and pig iron, the last either hot or cold. *Iron ore*

also is added, sometimes all the required amount at the beginning, but more usually only a part of it at first, and the rest after the slag is formed. The silicate slag, made up largely of calcium oxide from the limestone and silica from the ore, and of oxidized silicon from the pig iron, eventually rises and covers over the molten steel. The slag plays an important role in the steelmaking process.

Chemical reactions in the open hearth. When the melt has come up to a temperature of about 1600°, control of the chemical reactions begins. Some iron oxide, from the ore, has already dissolved in the slag, and more is added as it is needed. The iron oxide passes, by diffusion, from the slag into the melt underneath, where it dissolves in the liquid iron, and oxidizes the silicon and manganese first and then the carbon, just as in the Bessemer process. The oxides of silicon and manganese pass into the slag. The phosphorus, to the extent to which it is oxidized (probably to P_4O_{10}), is very likely locked in the slag by basic oxides, and the sulfur may in part be oxidized and escape as a gas or be locked in the slag. The carbon is oxidized,

$$C + FeO \longrightarrow Fe + CO$$

and the carbon monoxide may be given off so rapidly that the melt and slag appear to "boil." The diminishing carbon content is followed by frequent sampling and rapid analysis; and when the percentage of carbon has been dropped to the required value, the melt is ready for pouring. However, before the furnace is tapped, the alloying elements, or elements with special functions, may be added, in weighed amounts, such as manganese, aluminum, silicon, chromium, nickel, vanadium, tungsten, and molybdenum. The function of these elements will be described later.

Pouring. The slag is removed and the molten steel allowed to run out of the furnace into a large bucket-shaped vessel (lined with refractory brick) called a *ladle*. (Sometimes the alloying elements are added in the ladle rather than in the furnace.) At this stage two different pouring practices may be followed.

1. The steel may be poured, as it is, from the ladle into ingot molds to form what is called *rimmed steel*. In this case gas blowholes are formed in the solidified ingot. The reaction represented by the equation

$$C + FeO \rightleftarrows Fe + CO$$

is an equilibrium reaction, and the equilibrium is displaced toward the right as the steel cools. A very large quantity of carbon monoxide gas is set free—not all of which escapes from the ingot. The blowholes, however, are partially or entirely healed by later rolling or drawing operations, and rimmed steel is generally used to make deep-drawn shapes, such as sheets.

2. Before being poured from the ladle (or from the furnace) the steel may be *killed*, or *deoxidized*. This means that enough aluminum and silicon are added to combine with the oxygen of the FeO. These oxygen *scavengers* have a great affinity for oxygen, and their oxides are so stable that the production of carbon monoxide and of blowholes in the poured steel is minimized.

8. What is the significance of the words *acid* and *basic* in the terms *acid Bessemer* and *basic open hearth*?

9. Describe the chemistry of the open-hearth steelmaking process.

10. Distinguish between (*a*) iron and steel; (*b*) pig iron and cast iron; (*c*) wrought iron and steel; (*d*) carbon steel and stainless steel; (*e*) flux and slag; (*f*) austenite and ferrite; (*g*) tempering and casehardening; (*h*) graphite and cementite.

11. Carbon monoxide is a reducing agent. Why, then, in reducing iron ore in a blast furnace, is not all the carbon monoxide used, instead of allowing so large a quantity of it to remain in the exhaust gases from the furnace?

PROBLEMS

1. If we assume that 50 per cent of the coke used in a blast furnace is consumed as fuel and 50 per cent as a reducing agent, and if hematite is used as ore, will it be more economical to locate the blast furnace at the coal mine or at the ore mine?

2. If you wished to prepare a ton of steel containing 5 per cent of tungsten, how much ferrotungsten containing 80 per cent tungsten would be required?

CHAPTER 35

METALS: THEIR COMPOUNDS AND ALLOYS

Introduction · The term *metal* has two distinct meanings. (1) Chemists refer to metals as those elements whose atoms tend to lose electrons readily and form positive ions (cations) and whose hydroxides are basic or amphoteric. (2) In common usage the term *metal* is an old and familiar one, and refers to the above elements *in the free state.*

The uses of metals in modern times are so many and so varied that metal processing has become the backbone of the industrial life of a great nation such as the United States. The chemist's interest is in the methods by which the different metals are obtained from their ores (called metallurgy) and in the study of the properties of the metals and the reasons for their differences. About 75 per cent of the elements are metals; this is indicated in the table below.

PERIODIC TABLE SHOWING LOCATION OF METALS AND NONMETALS

METALS												NONMETALS					
H																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Rare-Earth Elements	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Actinide Series															

While the metals form cations and basic hydroxides, the nonmetals form negative ions (anions), and their hydroxides, in solution, are acids. These properties of nonmetals are in distinct contrast with those of the metals. There are borderline cases where the distinction between metal

than brittle, or a steel which is resistant to corrosion or to mechanical shock. These extreme properties or combinations of properties can be achieved by alloying the carbon steel with other elements. For example, the addition of chromium to steel makes it tough even while hard. Tungsten will keep a steel hard at high temperatures, and is used in high-speed tool steels. Nickel and chromium are the most widely used of all the alloying elements.

SOME ALLOY STEELS

PERCENTAGE COMPOSITION	PROPERTIES	USES
3.5 Ni	Hard, strong	Armor plate
3.5 Ni, 1.5 Cr 1.5 Ni, 0.6 Cr 1–1.5 Ni, 0.2–0.7 Cr *	Hard, tough, strong	Armor plate, projectiles, objects enduring shock or strain
17–18 W, 3.5–4.5 Cr, Co, Mo	Hard and temper-holding	High-speed lathe tools
12 Mn	Strong, tough	Burglarproof safes
13 Cr, 0.35 C	Rust-resisting	Stainless cutlery
17–19 Cr, 7–9.5 Ni, 0.11 C	Stainless, great strength	Rollers, furnace parts, plant equipment
0.1 Ti	Hard	Car rails and castings
0.2 V, 3.5 Ni, 0.75 Cr, 0.4 Mn	Fatigue-resisting	Automobile springs and axles
12–15 Si (Duriron)	Corrosion-resisting	Acid stills, electrodes
0.1 V	Tough	Automobile parts

*These are three standard nickel-chromium steels, the last one being made from a natural iron ore (Mayarí ore, Cuba) containing the three elements.

Since any number of these metals may be added together and in any proportion, it is possible to make a steel alloy with almost any given set of properties. Literally hundreds of these alloys have been made, and many of them have registered trade names, such as Duriron, a high-percentage silicon alloy that is very hard and brittle but resists acid corrosion. The remarkable hardness of such alloys as those of nickel, chromium, cobalt, tungsten, and vanadium arises in a manner similar to that previously noted for Fe_3C molecules. The "stranger" atoms intrude themselves between layers in the iron lattice and "key," or "lock," the layers together. The table above indicates the composition and properties of a few of the commonly used alloy steels.

Metallography · We have seen that the varieties of iron differ not only in chemical composition but also in physical structure. Much information concerning the structure of any sample of iron (and other metals as well) can be obtained from photomicrographs of carefully prepared specimens of the different varieties of iron. To prepare these, a cross section of the sample is made and

polished. This is then etched with some reagent such as nitric acid, which will react upon the different constituents of iron with different speeds. Photomicrographs are then taken of the resulting surfaces. This method of studying the structure of metals is known as *metallography*. Fig. 34-10 shows two typical photomicrographs of this kind.

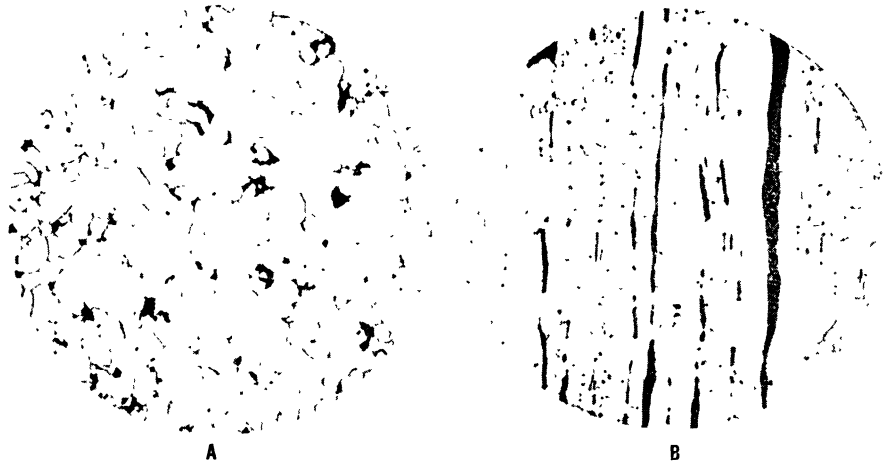


Fig. 34-10. Photomicrographs of a Sample of Low-Carbon Steel (A) and a Sample of Wrought Iron (B) · These two samples have nearly the same percentage composition, but their different methods of manufacture have resulted in entirely different physical structures with corresponding differences in properties. Note the long threads of slag in the wrought iron

QUESTIONS

1. (*a*) Outline the steps in the metallurgy of an ore. (*b*) What factors determine the use of any possible alternative methods? In your answer to *b* use the metallurgy of iron and sodium as examples.

2. Is there any relationship between the mineral resources of a nation and the wealth of the nation?

3. (*a*) What is the difference between a mineral and an ore? (*b*) Is crude petroleum an ore? (*c*) Is rock salt a mineral? (*d*) Is it an ore?

4. It is a difficult matter to prepare any one metal in a perfectly pure state. What reasons can you give for this?

5. (*a*) What are the functions of a blast furnace? (*b*) Describe in detail the blast-furnace process. (*c*) To what major uses are two products of the blast furnace put?

6. If you were operating a blast furnace, should you prefer to have the ore, coke, and limestone furnished to you in finely ground form, or in large lumps, or in pieces of medium size? Explain.

7. (*a*) Can steel of identical composition be made by the Bessemer and the open-hearth process? (*b*) Would there normally be any difference between the two products?

Summary of Chemical Properties of the Metals

Metals are electropositive in character; that is, the atoms of metals have relatively low attraction for electrons (in contrast with the atoms of nonmetals) and offer little resistance to the removal of the valence electrons to form positive ions. This property makes them reducing agents, and their strength as reducing agents varies with their attraction for electrons. They range in strength all the way from very strong reducing agents, such as the alkali metals (sodium, potassium), to very weak ones, such as the noble metals (gold, platinum). This variation is shown in the electrochemical series (p. 87).

The hydroxides of the metals are bases; metals may be defined as base-forming elements. The strength of a base is dependent upon the attraction of the metal ion for electrons: the smaller the attractive forces, the greater the tendency to ionize as OH^- ions and metal ions; and the larger the attractive forces, the less the tendency to ionize in this way, so that weaker bases are produced. The attraction for electrons becomes much greater when the oxidation state of an atom is increased and may become so great that the hydroxide ionizes as an acid. Manganous hydroxide, for example, forms Mn^{++} and OH^- ions, but in the oxidation state of + 7 manganese forms $HMnO_4$, which is an acid. Here the metal atom holds the oxygen atoms of the OH group, allowing the hydrogen ions to be ionized. In such an oxidation state the manganese is acting as a nonmetal. It is a general rule that, for the several oxidation states of an element, the higher the oxidation state, the more nonmetallic the element appears.

Many metal ions tend to form complex ions by means of co-ordinate covalent bonds. Some of the more common of these are $Cu(NH_3)_4^{++}$, HgI_4^{--}, and $Zn(NH_3)_4^{++}$. This property is particularly characteristic of the transition elements and is also related to the electron affinity of the ions.

A summary of a number of the chemical properties of the metals is shown in Fig. 35-3 (p. 626).

Compounds of the Metals

Preparation of Compounds of the Metals · A great many methods are employed in the preparation of compounds of the metals. These compounds, which include oxides, hydroxides, and salts, are very numerous, and each has its own peculiarities, which must be taken into account in

devising means for preparing it. In many cases some rather unusual method is employed, owing to the character of the minerals available in nature or to the accumulation of a cheap by-product in some industry.

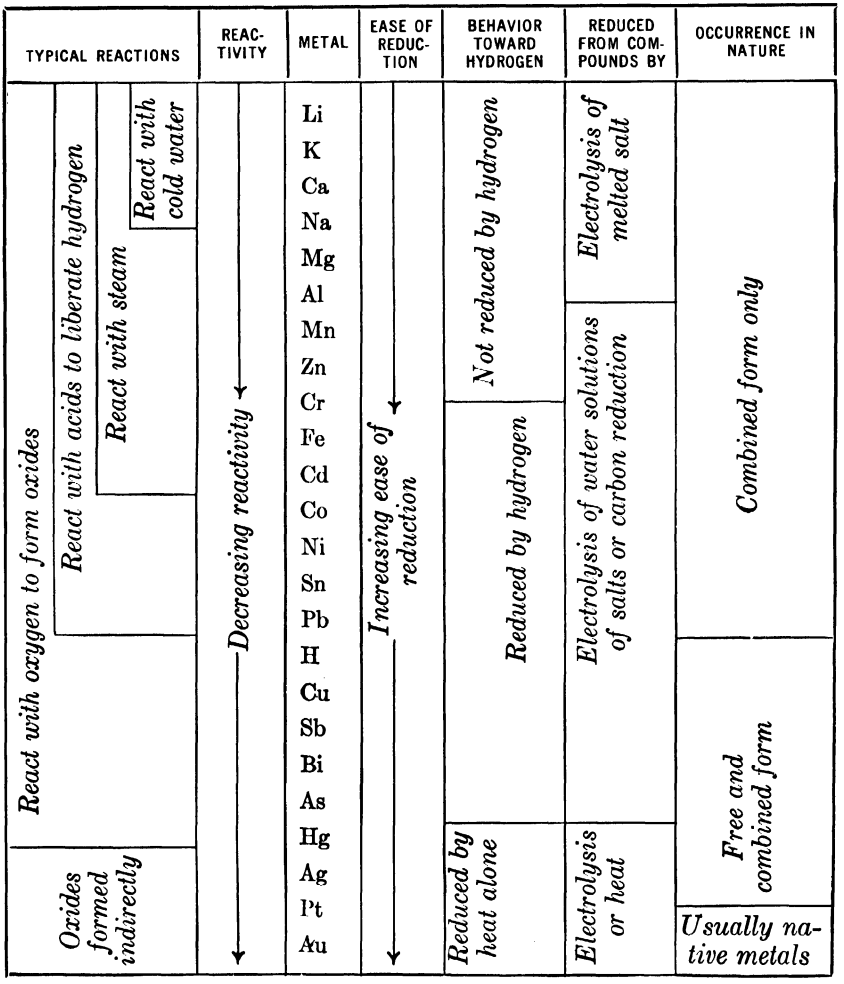


Fig. 35-3. Summary of General Chemical Properties of the Metals

Naturally the methods employed on a small scale in the laboratory are likely to differ from those used in the industries, where economy is the first requirement. There are, however, some general principles which underlie the great majority of these methods, a clear understanding of which will save time and effort in remembering the details in a given case.

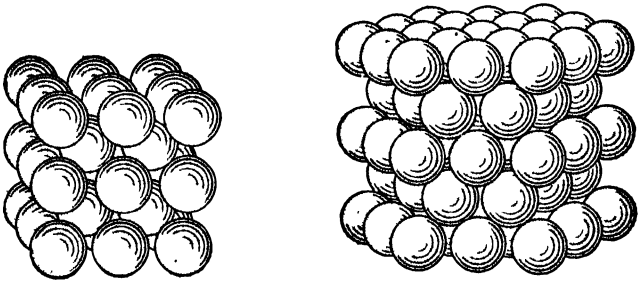
and nonmetal is not clear-cut; this is particularly true of the elements germanium, antimony, and tellurium (see table on page 622).

Properties of Metals · Metals may differ greatly among themselves in certain characteristics. We think of the metals as heavy bodies (high density), and most of them are; but a few, such as lithium and sodium, are lighter than water. All metals but mercury are solids at ordinary temperatures; cesium and gallium will melt on a hot day. Most metals are hard, and some are very hard; others, such as sodium and lead, can be cut with a knife.

The most general characteristics of metals are (1) high conductivity for electricity and heat and (2) the reflection of light in a characteristic way from a polished surface, described as *metallic luster*. These properties are not present in solid nonmetallic substances. One naturally inquires about the reason for this difference between metals and nonmetals, and looks for the explanation in the types of bonds between atoms in the metals.

Nature of the Metallic State · The atoms of those elements that have metallic properties possess few valence electrons, usually less than 4. In the vapor state the metals consist almost entirely of single atoms.

The arrangements of the atoms of metals in the solid state has been determined by the X-ray diffraction method (p. 184). The tiny, spherical atoms of the different metals arrange themselves in three of the ways in which balls can be packed regularly together in a box, namely, in lattices that are called *face-centered cubic* (already pictured on page 188), and *body-centered cubic* and *close-packed hexagonal* (Fig. 35-1).



A. Body-centered cubic B. Close-packed hexagonal

Fig. 35-1. Typical Metallic Structures · These two lattices, and the face-centered cubic of Fig. 11-29 (p. 188), are three of the four possible ways in which spheres can be arranged in a regular pattern

Examples of metals that crystallize in these different types of lattices are

Face-centered cubic: copper, silver, gold, calcium, aluminum, lead, platinum.
Body-centered cubic: lithium, sodium, potassium, rubidium, cesium, barium.
Close-packed hexagonal: zinc, cadmium, beryllium, magnesium.

Each atom is in contact with a number of similar atoms (8, 12, and 12, in the lattices above). The valence electrons are mobile and free to roam through the body of the metal; nevertheless they act effectively to bind atom to atom. The bonds so formed are called metallic bonds. This bonding is very different from the bonding between the positive and negative ions in a crystal of a salt, held together by strong electrostatic forces, or from the van der Waals forces that hold molecules in a crystal of sugar or carbon dioxide (p. 73), or from the strong covalent bonds that bind together the carbon atoms in a diamond, making the crystal one large molecule (p. 350).

It is the mobility of the valence electrons that gives the metals their *distinctive* property of high electrical conductivity. *All* the current is carried by the moving electrons, *none* by moving metallic atoms. This is in sharp contrast with conduction in a solution of an electrolyte, in which the current is carried by the movement of cations and anions.

This same electron mobility within a metal is responsible for the metallic luster common to all metals, for such electrons tend to absorb light and re-emit it, rather than transmit light. Furthermore, the metallic bonds between atoms make the deformation of many metals possible, without fracture; for the displacement of the atoms in the mobile-electron atmosphere would not disturb the attractive forces as much as would the displacement of the atoms in an ionic or atomic crystal. Metals tend to be ductile and malleable, whereas the nonmetallic elements are nonductile and brittle.

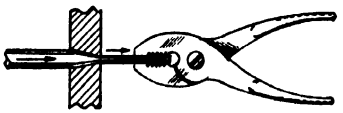


Fig. 35-2. Reducing the Size of a Metallic Wire by Drawing It through a Tapered Hole. Illustrates the ductility of a metal

Properties of Metals Variable · The physical properties of metals are greatly modified by the presence of even small percentages of impurities. A very little arsenic greatly reduces the electrical conductivity of copper; a few tenths of 1 per cent of carbon changes soft iron into steel.

The physical properties are modified also by the mechanical treatment to which a metal has been subjected. When cooled from the liquid state under proper conditions, a given weight of metal may be obtained as a continuous, *single* crystal; but ordinarily it will freeze into an enormous number of separate *crystal grains* because crystallization will start at many points. The properties of the solid metal will depend on the size of these grains, on the heat treatment during cooling (annealing and tempering), and on the mechanical treatment (rolling and forging). Consequently, in giving exact numerical values for some of the properties of the metals, it is necessary to state the conditions of treatment.

Insoluble Compounds · It is evident that a knowledge of the solubility of compounds is an important part of a training in chemistry (Chap. 12). With this knowledge it is possible, in many cases, to predict the course of a reaction and to devise ways in which to prepare desired compounds. For precise information a dictionary of solubilities must be consulted, but it is possible to make a few general statements which will be of assistance in understanding the reactions described in the following chapters. These statements apply only to normal salts of the more familiar metals. Acid salts are likely to be more soluble than normal salts, and basic salts less so.

1. **Hydroxides.** All hydroxides are insoluble in water except those of ammonium, sodium, potassium, calcium, strontium, and barium.

2. **Nitrates.** All nitrates are soluble in water.

3. **Chlorides.** All chlorides are soluble in water except silver and mercurous chlorides. (Lead chloride is but slightly soluble.)

4. **Sulfates.** All sulfates are soluble in water except those of barium, strontium, and lead. (Sulfates of silver and calcium are only moderately soluble.)

5. **Sulfides.** All sulfides are insoluble in water except those of ammonium, sodium, and potassium. The sulfides of calcium, strontium, barium, and magnesium are insoluble in water but are changed by hydrolysis into acid sulfides which are soluble. On this account they cannot be prepared by precipitation.

6. **Carbonates, sulfites, phosphates, and silicates.** All these normal salts are insoluble in water except those of ammonium, sodium, and potassium. Magnesium carbonate is slightly soluble.

For further information concerning the solubilities of compounds of the metals, consult the table in the Appendix.

Double and Complex Salts

On preceding pages a number of compounds have been represented by formulas which indicate that they are made up of a combination of two different salts. The formula of cryolite is often written $AlF_3 \cdot 3\,NaF$; potassium fluosilicate was formerly given the formula $SiF_4 \cdot 2\,KF$; and alum, often written $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$, is another example of the same general character. Among these salts two extreme cases can be defined.

1. ***Double Salts*** · Carnallite ($KCl \cdot MgCl_2 \cdot 6\,H_2O$), a well-defined crystalline compound, is a good example of a *double salt.* When it is dissolved in water, the solution acts as though it contained a mixture of the

chlorides of potassium and magnesium, both of which are freely ionized. Silver nitrate precipitates all the chlorine as silver chloride; ammonium phosphate precipitates the magnesium as magnesium ammonium phosphate ($MgNH_4PO_4$). *A salt of this kind, which in solution decomposes into its constituent salts and gives reactions for their individual ions, is called a double salt.*

2. ***Complex Salts*** · Potassium fluosilicate (K_2SiF_6) may be taken as an example of a *complex salt.* It can be prepared by bringing together in solution the fluorides of potassium and silicon:

$$2\,KF + SiF_4 \longrightarrow K_2SiF_6$$

The product of the reaction cannot properly be regarded as a double salt, for it gives none of the reactions characteristic of the fluorides from which it is formed. Thus, when calcium chloride is treated with potassium fluoride, calcium fluoride precipitates. With fluosilicates, on the other hand, no precipitation occurs on adding calcium chloride, showing that fluoride ions are not present. Instead, the complex ions SiF_6^{--} are present, and take part in all the reactions of the fluosilicates. The fluosilicates must then be regarded as salts of fluosilicic acid (H_2SiF_6) rather than as made up of two different fluorides, as in the case of double salts. *Compounds of this kind, which yield ions other than those of the salts from which they may be formed, are called complex salts.*

Alloys of the Metals

Alloys of Metals · A few of the metals, such as copper and aluminum, find large uses in very pure form. *Pure* iron is rarely used, but a vast amount of *nearly* pure iron is used (Chap. 34). In the great majority of cases the metallic objects that we use or see every day are made not of *one* metal but of two or more metals melted together and called *alloys.* For example, gold jewelry, silver plate, coins of all kinds, brass, bronze, and pewter objects, and most objects of iron (such as automobile parts) are alloys.

The Nature of Alloys · When two melted metals are mixed together, they act much like any other pair of liquids. (1) Some melted metals mix in all proportions, like sulfuric acid and water, and this is the case with lead and antimony. (2) Some may have a limited solubility, each in the other (like ether and water). In this case the mixture separates into two layers, both saturated solutions, the lighter floating on the heavier. Lead and zinc are a pair of this kind. (3) Some may combine in various proportions to form definite compounds, more or less soluble in the excess

1. **Direct union of two elements.** Very many binary compounds may be prepared by heating the metal with the appropriate nonmetal. Among these are oxides, sulfides, and halides. The product in such cases is, of course, anhydrous, and this method finds wide application when it is the *anhydrous* rather than the *hydrated* compound that is wanted. The method is most frequently employed in the preparation of anhydrous halides, as, for example, aluminum chloride:

$$2\ Al + 3\ Cl_2 \longrightarrow 2\ AlCl_3$$

2. **Treatment of a metal or its oxide, hydroxide, or carbonate with an acid.** Many of the metals are produced commercially in a high degree of purity and at small cost, and these are often the most convenient starting point for the preparation of their compounds on a laboratory scale. For example, the salts of zinc and copper are frequently made in this way:

$$Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2\uparrow$$
$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + 2\ H_2O + SO_2\uparrow$$

In the industries the hydroxide, oxide, or carbonate is more likely to be employed, since it is usually found in nature or is easy to prepare. For example, calcium salts are often prepared from lime (CaO), as in the case of the nitrate:

$$CaO + 2\ HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$

3. **Decomposition of a compound.** The decomposition of a compound, either by heat alone or aided by a reducing agent, frequently leads to the formation of simpler substances. For example, nitrates, carbonates, and hydroxides, when heated sufficiently, usually yield oxides:

$$2\ Cu(NO_3)_2 \longrightarrow 2\ CuO + 4\ NO_2\uparrow + O_2\uparrow$$
$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$
$$2\ Al(OH)_3 \longrightarrow Al_2O_3 + 3\ H_2O\uparrow$$

4. **Reduction.** When heated with carbon, a salt of an oxygen acid is usually reduced and yields a binary compound of the metal with the acid-forming element. For example, sulfates yield sulfides, and phosphates yield phosphides, as shown in the equations

$$BaSO_4 + 4\ C \longrightarrow BaS + 4\ CO\uparrow$$
$$FePO_4 + 4\ C \longrightarrow FeP + 4\ CO\uparrow$$

5. **Displacement of a volatile acid.** When a nonvolatile acid acts upon a salt of a volatile acid, the latter is displaced in accordance with the general principles of equilibrium, *provided the volatile acid is only sparingly*

soluble in any liquid that may be present. For example, the reaction of sulfuric acid with sodium chloride goes on to completion if the sulfuric acid employed is quite concentrated, for hydrogen chloride is only slightly soluble in this liquid:

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$$

In dilute solution the reaction results in an equilibrium, for in this case the hydrogen chloride is freely soluble in the solution.

6. **Methods based upon precipitation.** The formation of a precipitate when two electrolytes are brought together in solution takes place in accordance with the principles of ionic equilibrium developed in Chapter 25. *In general, it may be said that when two salts, or a strong acid and a salt, are brought together in solution, double decomposition takes place, with the formation of a precipitate if the union of any pair of ions produces an insoluble salt.* When a salt of a strong acid is treated with a *weak* acid, however, no precipitate is formed, even though double decomposition would result in the formation of an insoluble salt, unless the latter is extremely insoluble. It has also been shown that the *salts of strong acids,* such as sulfates or chlorides, when insoluble in water, *are also insoluble in dilute acids. Salts of weak acids,* such as carbonates, sulfites, and sulfides, though insoluble in water, *are soluble in dilute acids.* These principles are of constant application in the preparation of compounds.

7. **Fusion reactions.** When compounds are melted together, it sometimes happens that a double decomposition occurs which would not take place if the same salts were brought together in water. In such fusion reactions one of the melted salts may be regarded as the solvent, and it is to be expected that the solubility of the other in this solvent will be different from its solubility in water. For example, barium sulfate is less soluble in water than barium carbonate is, and consequently it is not greatly affected by aqueous solutions of sodium carbonate. *In melted sodium carbonate,* on the contrary, it is readily soluble, while barium carbonate is insoluble. As a consequence, when it is melted together with sodium carbonate, the following double decomposition takes place:

$$BaSO_4 + Na_2CO_3 \longrightarrow BaCO_3\downarrow + Na_2SO_4$$

When the mixture is cooled and then digested with warm water, the sodium sulfate dissolves, leaving the barium carbonate, which may then be filtered off and converted into any desired salt. This forms a convenient method of passing from an insoluble salt of a strong acid to a similar salt of a weak acid. It will be recalled that natural silicates can be decomposed in the same way.

average of those of the constituent metals. It seems entirely reasonable that the color of brass should be golden, since it is composed of reddish copper and silvery zinc; but silvery nickel almost completely overcomes the color of copper, as is evident in our five-cent coins (75 per cent copper, 25 per cent nickel), and both silver and cadmium give gold a greenish tint, though they are silvery in color.

As we have seen, the freezing point of an alloy composed of two metals is usually below that of either component if the metals form a simple eutectic; but if they form solid solutions, the temperature at which solidification is complete may be at some intermediate point. As a rule, an alloy is harder than either component, and the electrical conductivity is less. For this reason most kinds of resistance wires are alloys. Many alloys (for example, stainless steel, Chap. 34) resist chemical corrosion better than their components taken separately, so that alloys find increasing use in chemical industries.

If a nonmetal such as boron, silicon, or phosphorus is one of the components of an alloy, the properties become even less predictable.

Future of Alloys · A considerable number of alloys have been in common use for a very long time. Among these are brass, bronze, pewter, solder, type metal, and coinage metals. Some of these long ago became more or less standardized in composition because their uses formerly were rather definite. The period of diversified machinery, especially electric devices, does not date back much beyond half a century, and the call for metal materials to meet an ever-increasing variety of purposes is very insistent, so that the production of new alloys adapted to exactly specified purposes has become one of the most important problems for the metallurgist and chemist. Some large firms do nothing but manufacture alloys guaranteed to have almost any specified properties; they make metal bodies to order.

It should be remembered that there are many metals which as yet have found no important uses in pure condition and whose alloys have been little studied, that almost any number of metals and even some nonmetals can be combined in an alloy, and that the relative proportions of each can be varied within wide limits. It will then be seen that the field of alloys is a rich and fascinating one for the scientist, as well as for the inventor.

Alloys of Antimony and Bismuth · By way of illustration it will be well to describe briefly some of the alloys of antimony and bismuth—two metals described in Chapter 23. Other alloys will be referred to in succeeding pages in connection with the various metals.

Antimony and bismuth are both very heavy, low-melting metals, and some of their alloys melt at a still lower temperature. Bismuth has the somewhat unusual property of expanding in the act of solidification, and many of its alloys share this property. This is an important property in making type; for the cast type in expanding fits the mold tightly, and the fine lines are emphasized in the

cast and not obliterated, as would occur if contraction took place. Many of these alloys are fairly hard and take a smooth polish. They are much used for bearings in machinery. Bismuth is a component in a number of very low-melting alloys which are used as safety links or plugs in fire curtains, boilers, and fuses.

SOME COMMON ALLOYS CONTAINING ANTIMONY OR BISMUTH

NAME	LEAD (Per Cent)	TIN (Per Cent)	ANTIMONY (Per Cent)	BISMUTH (Per Cent)	COPPER (Per Cent)
Type metal	70	10	18		2
Britannia metal		91–85	9–11		0.2–1 (Zn, 0–3)
Pewter	0–20	89–74	0–7.6		0–3.5
Babbitt metal (genuine)		89	7.3		3.7
White metal* (tin base)	12–40	74–42	9.5–16		1–4.2
White metal* (zinc base)	Zn, 88	2	2		8
Rose's metal (mp, 93.8°)	28	22		50	
Wood's metal (mp, 60.5°)	25	12.5		50	Cd, 12.5
Newton's metal (mp, 94.5°)	31	19		50	

**White metal* is a general term for a large group of alloys, of which the two listed in the table above are examples.*

Passive Metals · Iron readily dissolves in both dilute and concentrated nitric acid; but when it is brought into contact with fuming nitric acid, that is, with nitric acid containing nitrogen dioxide in solution, it loses many of its characteristic properties and is then said to be in a *passive state* (Fig. 35-5). For example, such iron is no longer attacked by dilute nitric acid, nor does it precipitate copper and silver from solutions of their salts, as does ordinary iron. The metal loses its passivity when it is rubbed, scratched, or given a sharp blow, or when certain other metals are brought into contact with it. A number of other metals, including cobalt, nickel, and chromium, act in a similar way. No entirely satisfactory explanation has been offered to account for this phenomenon. Possibly the passivity is due to the presence of a protective film of oxygen on the surface of the metal.

Corrosion of Metals · Metals exposed to the elements tend to be attacked at the surface, forming compounds; this process of *corrosion* weakens the metal structure. One of the great problems of industry is the prevention of such corrosion. Some metals, such as aluminum and chromium, do not corrode or rust because they form a layer of oxide on the surface which prevents further attack. Iron, except when very pure, corrodes, or *rusts*, readily, especially in the presence of moist air containing carbon dioxide and oxygen. An explanation of the rusting process is as follows: The impurities in the iron form small, local, electrochemical cells (Chap. 13) with the iron. In such a cell the iron tends to give off electrons to form ferrous ions (Fe^{++}), and hydrogen ions from the water may gain electrons to form hydrogen molecules:

$$Fe + 2\,H^{+} \longrightarrow Fe^{++} + H_2$$

liquid. (4) Some may be practically insoluble in each other, like oil and water. As the melt cools, the crystals that form may be pure metals, solid solutions of one metal in the other, compounds, or mixtures of any of these. Thus alloys exhibit great variety in nature and in structure.

Solid Solutions · In some cases two melted metals mix in all proportions, and the crystals that separate on cooling contain the two metals in about the proportions in which they were present in the melt. Such crystals are called *solid solutions* because, though they closely resemble liquid solutions, they are solids.

Thus, when zinc and copper are melted together, as a rule in the proportion of about one atom of zinc to two or three of copper, and the solution is allowed to cool and crystallize, we obtain *brass*. X-ray analysis shows that brass of this composition crystallizes in a lattice like that of copper, but that the zinc atoms have replaced some of the copper atoms, generally at the corners of the cubes of the lattice. Therefore brass is not a mixture of tiny crystals of zinc and of copper, but is a far more fine-grained mixture of the actual atoms themselves. Zinc atoms are *dissolved* in the lattice of the copper atoms.

The Eutectic · Let us now consider the simplest case of a cooling melt containing two metals, namely, the case where the crystals that form are the pure metals. If we add a little antimony to melted lead, the antimony dissolves in the lead. When the solution is cooled slowly, we find that crystals of pure lead separate, and that the temperature at which crystal formation begins is below the melting point of pure lead. The situation is similar to that which occurs when a solid solute dissolves in water; when the solution is cooled, pure ice freezes out, and the freezing point of the solution is below that of pure water. In the case of the metals, however, either metal can act as the solvent; and if we add a little lead to melted antimony and cool the solution, crystals of *pure antimony* form below the melting point of antimony. Each of these metals lowers the solidifying point of the other. The more of the solute metal we add, the lower is the temperature of crystal formation.

It is evident that if we melt the two metals together in every possible proportion, we shall obtain one particular mixture that will have a lower solidifying point than any other. At this lowest freezing point, crystals of *both* metals are deposited side by side. This mixture is called the *eutectic* of the two metals, and its melting point (or freezing point) is called the *eutectic temperature*. At this temperature the proportion of the two metals in the melt and in the mass of depositing crystals is the same and is constant for a given pair of metals. In physical structure the eutectic is a fine-grained conglomerate of crystals of the two metals.

Eutectic diagram. In the diagram (Fig. 35-4) let us indicate the composition of the alloy along the line AB divided into 100 divisions. Let $A = 100$ per cent antimony and $B = 100$ per cent lead. C, for example, which is halfway between A and B, will then represent 50 per cent each of antimony and of lead.

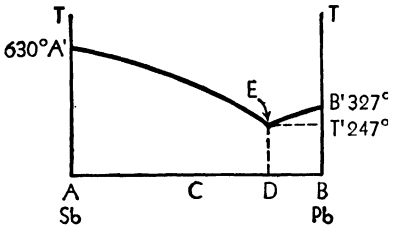


Fig. 35-4. Diagram Illustrating the Eutectic of Antimony and Lead

The vertical lines AT and BT represent temperature, A' being the melting point of antimony and B' that of lead. If to pure lead we add a small percentage of antimony, the freezing point is lowered, the fall with increasing quantities of antimony being shown by the sloping line $B'E$. Similarly, if to pure antimony we add increasing quantities of lead, the fall in freezing point is shown on the sloping line $A'E$. The point E is thus the lowest temperature at which any mixture of antimony and lead can remain liquid, and is therefore the *eutectic temperature*. The composition, D, of the liquid at this point (E) is called the *eutectic composition*, and is 80 per cent lead and 20 per cent antimony, in this case. A eutectic mixture melts and freezes at a perfectly definite temperature, like a pure metal.

This discussion of the behavior of a melt on cooling applies only to the case in which the *pure metals* separate as crystals. Compounds of metals, as well as solid solutions, also form in many cases, as mentioned above. But we shall not consider these more complicated systems.

Structure of Alloys · When we cool a melted mixture of metals, one or the other pure metal or a compound or a solid solution at first separates. As the temperature falls, the crystals of these solids grow in size and in number, the composition of the remaining liquid changing as a result, until finally the eutectic temperature is reached and the liquid has the eutectic composition. At this temperature the entire remaining liquid slowly solidifies as a mass of very small, intimately mixed crystals of the various components present.

It will be seen that if no precautions are taken, the solid alloy is likely to consist of rather large crystals of some kind embedded in a fine matrix of small eutectic crystals. Such a structure is unsuited to many technical uses. Rapid cooling tends to keep all crystals small and well mixed; and the nearer the composition of the alloy approximates a eutectic, the more homogeneous will be the structure. Some solid solutions are relatively free from the tendency to form large crystals, and are homogeneous in structure.

Properties of Alloys · In general, the properties of an alloy of two metals cannot be predicted with any certainty from those of its constituent metals, though some properties, such as density, are apt to be a rough

CHAPTER 36

THE ALKALINE-EARTH METALS

Introduction · The group of elements beryllium, magnesium, calcium, strontium, barium, and radium constitute family IIA of the elements (see the periodic table, p. 313). The elements of this family are sometimes called the alkaline-earth metals because they resemble the alkali metals, and their oxides resemble the "earths" (such oxides as those of iron and aluminum). The properties of these elements are found to be those that we should predict from a knowledge of their electron configurations and atom sizes (see Fig. 36-1 and the table below).

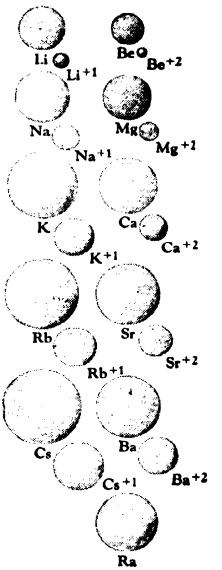


Fig. 36-1. Relative Sizes of the Atoms and Ions of the Alkali and Alkaline-Earth Metals

The atoms of these elements, from top to bottom of the group, are almost the same size as those of the alkali family (Fig. 36-1). They contain 2 valence electrons, and the relatively low electron affinity resulting from the large atom size makes it possible to strip off these electrons readily. Hence they are active metals and are found high in the electrochemical series. They all (1) tarnish when exposed to air, (2) react slowly with water, (3) form compounds with all the common nonmetals, and (4) have an electrovalence of +2. Owing in part to the smaller ion size and to the double charge (+2) on the ion, several of their compounds are insoluble (p. 629).

Beryllium and magnesium have much the smallest atoms and are the least basic of the elements of the group.

All these elements have a gray-white metallic luster and may be ham-

SOME PROPERTIES OF THE ALKALINE-EARTH METALS

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	FIRST PREPARED BY	VALENCE	ATOMIC DIAMETER (Å)	ELECTRONS IN SHELLS
Beryllium (Be)	9.02	4	1.8	1350°	Wöhler, 1828	+2	2.22	2, 2
Magnesium (Mg)	24.32	12	1.74	651°	Davy, 1808	+2	3.20	2, 8, 2
Calcium (Ca)	40.08	20	1.55	810.0°	Davy, 1808	+2	3.94	2, 8, 8, 2
Strontium (Sr)	87.63	38	2.6	800.0°	Davy, 1808	+2	4.30	2, 8, 18, 8, 2
Barium (Ba)	137.36	56	3.5	850.0°	Davy, 1808	+2	4.34	2, 8, 18, 18, 8, 2
Radium (Ra)	226.05	88	5	960.0°	Curie, 1896	+2	4.40	2, 8, 18, 32, 18, 8, 2

mered and rolled. Barium is as soft as lead, whereas beryllium is hard enough to scratch glass.

Occurrence · The high activity of these elements makes unlikely their occurrence in the *free state* in nature. Compounds of calcium and magnesium are very abundant in nature. The distribution of these elements in igneous rocks is given in the following table:

DISTRIBUTION OF THE GROUP II, A, METALS IN IGNEOUS ROCKS

ELEMENTS	PER CENT IN IGNEOUS ROCKS
Calcium	3.63
Magnesium	2.09
Barium	.05
Strontium	.0002
Beryllium	.00001
Radium	10^{-12}

Some of the more common minerals in which these metals are found are indicated in the following table:

SOME COMMON MINERALS CONTAINING THE ELEMENTS OF GROUP II A

METAL	MINERAL	
	Name	Formula
Beryllium	Beryl	$3\,BeO \cdot Al_2O_3 \cdot 6\,SiO_2$
Magnesium	Magnesite	$MgCO_3$
	Talc, or soapstone	$H_2Mg_3(SiO_3)_4$
	Asbestos	$CaMg_3(SiO_3)_4$
	Dolomite	$MgCO_3 \cdot CaCO_3$
	Spinel	$Mg(AlO_2)_2$
	Carnallite	$MgCl_2 \cdot KCl \cdot 6\,H_2O$
Calcium	Calcite	$CaCO_3$
	Gypsum	$CaSO_4 \cdot 2\,H_2O$
	Fluorspar	CaF_2
	Fluorapatite	$CaF_2 \cdot 3\,Ca_3(PO_4)_2$
Strontium	Strontianite	$SrCO_3$
	Celestite	$SrSO_4$
Barium	Barite	$BaSO_4$
	Witherite	$BaCO_3$
Radium	Usually in uranium ores, Chap. 19	

Both magnesium and calcium compounds are found in sea water and other natural waters, and in plant and animal tissue.

The presence of carbon dioxide gives electrolytic properties, and the oxygen oxidizes ferrous ions,

$$4\ Fe^{++} + 10\ H_2O + O_2 \longrightarrow 4\ Fe(OH)_3 + 8\ H^+$$

and combines with and removes any hydrogen formed on the surface of the metal; hence both carbon dioxide and oxygen accelerate the rusting process. Apparently rust consists of the porous hydroxide, $Fe(OH)_3$, thus formed, combined with a variable amount of water. Pitting, or uneven rusting, results from an uneven distribution of oxygen over the surface of the iron, which permits the rate of rusting to vary.

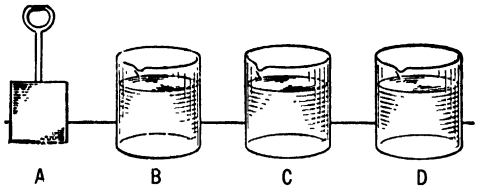


Fig. 35-5. Diagram Illustrating the Preparation and Properties of Passive Iron · The passivity of iron may be illustrated in the following simple way: A piece of sheet iron, *A*, is immersed for a few moments in fuming nitric acid contained in *B*. It is next lowered into pure water in *C*, in order to wash off the adhering acid. Finally it is dipped for a moment into a solution of copper sulfate in *D*. Apparently no change takes place. If now the iron is struck a sharp blow, it at once loses its passivity and regains its normal property of replacing copper from copper sulfate, as is evidenced by the rapid formation of a thin film of copper over the entire surface of the iron

Rusting is of enormous economic importance, since it is estimated that some $3,000,000,000 is annually lost through the rusting of iron and steel. We may seek to diminish rusting (1) by searching for an alloy that is rust-resisting; (2) by depositing upon the surface of the iron a film of some glaze, (enamel ware, p. 771), or of some metal that is not acted upon by moist air (tinning, galvanizing); (3) by the use of various paints; (4) by heating the iron object and forming upon its surface a film of magnetic oxide (Fe_3O_4), which is not porous and protects the metal (Russia iron, gun barrels).

QUESTIONS

1. How can you distinguish between metals and nonmetals in terms of their relative electron affinities?

2. Detail the general physical characteristics of the metals, and contrast the chemical properties of the metals and the nonmetals.

3. Give the meaning of the following terms: (*a*) *metallic luster;* (*b*) *malleable;* (*c*) *single crystal;* (*d*) *crystal grain;* (*e*) *alloy;* (*f*) *eutectic;* (*g*) *electrolysis.*

4. What cases can you cite of compounds formed between two nonmetals? (*b*) Are metallic compounds ever formed in an alloy?

5. Why should alloys be superior to pure metals for many purposes?

6. Suggest a method for preparing each of the following compounds: (*a*) ferrous sulfate ($FeSO_4$); (*b*) silver sulfide (Ag_2S); (*c*) silver bromide (AgBr); (*d*) copper chloride ($CuCl_2$).

7. (*a*) Lead chloride is insoluble in acid solutions. What inference can you draw as to the strength of hydrochloric acid? (*b*) When lead chloride is heated with concentrated sulfuric acid, the products are lead sulfate and hydrogen chloride. How do you explain this?

8. Ferrous oxalate (FeC_2O_4) is insoluble in water. (*a*) When ferrous chloride ($FeCl_2$) and oxalic acid ($H_2C_2O_4$) are brought together in solution, only a part of the iron is precipitated as oxalate. Why? (*b*) The addition of ammonium hydroxide causes complete precipitation. Why?

9. Distinguish between double and complex salts; give examples of each.

PROBLEMS

1. One liter of water dissolves 8.35 g of silver sulfate at 25°. (*a*) Express this solubility in terms of gram-formula weights per liter. (*b*) Assuming complete ionization, express the concentration of each ion in terms of gram-ionic weights per liter.

2. (*a*) In what three ways could you prepare 100 g of cupric chloride ($CuCl_2$)? (*b*) What weight of the copper-containing material will be required in each case?

3. One hundred grams of calcium carbonate ($CaCO_3$) is decomposed by heat. (*a*) What are the resulting products? (*b*) Calculate the weight of each.

4. What weight of copper sulfate ($CuSO_4$) can be prepared from 1000 g of copper?

Spectra · Several of the alkaline-earth metals ionize readily at the temperature of a Bunsen flame to impart characteristic colors to the flame; the calcium flame is brick-red, strontium bright crimson, barium green, and radium crimson. When the flames are viewed through a spectroscope, the characteristic spectral lines appear. Beryllium and magnesium do not color a Bunsen flame.

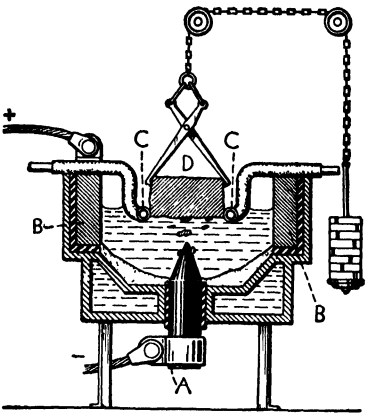


Fig. 36-2. Electrolytic Cell for the Production of Calcium · The cell consists of a cylindrical vessel through the bottom of which extends an iron cathode, *A*. The anodes, *B*, *B*, several in number, are distributed about the sides of the vessel. The calcium separates at the cathode as a liquid and rises in the form of globules to the lower surface of a solid stick of calcium, *D*, suspended above the cathode, as shown in the diagram. There it becomes chilled by a water-cooling device, *C*, *C*, and adheres to the stick of calcium, which is slowly raised as it increases in length

Preparation · The reduction process in the metallurgy of these metals is usually carried out by the electrolysis of their molten chlorides or fluorides in the presence of other chlorides to lower the melting point of the salt. A special cell for the preparation of metallic calcium is described in Fig. 36-2.

Beryllium melts at a very high temperature; this necessitates the use of an electrolyte which is a high-melting mixture of three fluorides: those of beryllium (BeF_2), an alkali metal, and an alkaline-earth metal. As the beryllium is deposited at the cathode, fluorine is set free at the anode.

Magnesium melts at a much lower temperature, and the electrolyte used may be anhydrous magnesium chloride ($MgCl_2$); a common commercial electrolyte is 70 per cent magnesium chloride and 30 per cent sodium chloride. Magnesium is liberated at the cathode, floats on the electrolyte, and is skimmed off. Chlorine is evolved at the anode. Magnesium may be prepared also by heating the oxide to high temperatures with coal dust or silicon and distilling off the magnesium vapor.

Uses of the Metals · Pure beryllium has no commercial use, but it forms alloys which have become very important in recent years. Magnesium alloys have *lightness* and *high tensile strength*, and consequently are used extensively in the construction of airplanes, portable tools, and other things which have need of these properties.

The alkaline-earth metals, as well as aluminum, are used in vacuum tubes as "getters" to remove the last traces of oxygen, nitrogen, and water vapor (p. 740), through chemical combination of the metals with the gases. An alloy of barium,

strontium, and magnesium is often used for this purpose. Small percentages of barium alloyed with nickel form the wire in many spark plugs. Calcium and barium are used in various bearing metals, and as "scavengers" to remove gases from melted metals.

Historical. As in the case of the alkalies, the alkaline earths were thought to be elementary in character until 1808, when Davy succeeded in decomposing them, just as he had decomposed the alkalies. In a lecture delivered on June 30, 1808, before the English Royal Society, Davy refers to his discovery as follows: "The evidence for the composition of the alkaline earths is then of the same kind as that for the composition of the common metallic oxides; and the principles of their decomposition are precisely similar, the inflammable matters in all cases separating at the negative surface in the voltaic circuit, and the oxygen at the positive surface. These new substances will demand new names; and on the same principles as I have named the bases of the fixed alkalies I shall venture to denominate the metals from the alkaline earths barium, strontium, calcium. . . ."

Beryllium was discovered twenty years later by Wöhler, and radium by Madame Curie in 1896.

Beryllium and Its Compounds

The Metal · Beryllium is one of the latest additions to the list of light industrial metals, one of the lightest of those in this group, and the hardest to get. As yet it has practically no uses as a pure metal but is used wholly in alloys. It is a hard, high-melting metal and adds hardness and strength to other metals, particularly to copper. The chief alloy of beryllium is a copper alloy containing about 2.25 per cent of beryllium. This alloy is golden in color, has great tensile strength, and can be heat-treated to produce remarkable springs that show no "fatigue" with use. A similar alloy with nickel makes a high-melting, smooth bearing metal, especially adapted to the demands of aircraft engines. In small percentages beryllium improves many varieties of rustless steel that contain nickel, cobalt, or chromium.

Beryllium burns when heated in air or oxygen to form the monoxide, dissolves readily in acids, and reacts with alkali hydroxides to produce hydrogen, as indicated in the equation

$$Be + NaOH + H_2O \longrightarrow NaHBeO_2 + H_2$$

Compounds of Beryllium · Beryllium forms a series of compounds resembling in formulas the corresponding compounds of the other members of the magnesium family. The hydroxide, $Be(OH)_2$, is insoluble in water but is amphoteric and therefore dissolves in both acids and alkalies. The oxide, BeO, is as hard as emery, does not react with water, and melts at about 2500°. It is prepared from the mineral beryl and is used in making

refractory crucibles. Beryllium silicate is used in some dental cements and as a coating for some fluorescent-light bulbs. The salts of beryllium readily hydrolyze and form basic compounds. The soluble compounds of the element are reported to have a sweetish taste; but some evidence indicates that the metal or its compounds may be very dangerously poisonous.

Magnesium and Its Compounds

The Metal · Magnesium is one of the "light" metals that have become so important in industry, owing to the need for the use of metals lighter than iron and steel. It is only about one-fifth as heavy as iron and two-thirds as heavy as aluminum.

DENSITIES OF FOUR COMMON METALS

ELEMENT	DENSITY
Beryllium	1.8
Magnesium	1.74
Aluminum	2.70
Iron	7.86

Magnesium is a silvery metal that tarnishes to a dull-gray surface through oxidation. It is used almost entirely as an alloy metal. In this country the development of magnesium alloys began about 1920, and the best-known ones are called *Dowmetals*. They contain from 85 to 99 per cent of magnesium, and are light, strong, easily machined, and water-resisting. They can be cast, forged, rolled into plates, drawn into rods, or pressed into tubes; and they are especially useful in replacing copper or iron where lightness is important, as in the body structure of aircraft, in home appliances, and in machine parts such as the pistons in gas engines.

Reactions of Magnesium · Magnesium burns with a brilliant flame to form the monoxide; in air a small amount of the nitride is also formed. The light emitted is rich in ultraviolet rays; this accounts for the use of magnesium in photographic flash bulbs. At room temperature magnesium reacts very slowly with water to produce hydrogen, but at the ignition temperature of the metal it reacts vigorously with both water and carbon dioxide. It dissolves readily in acids.

Compounds of Magnesium · The compounds of magnesium are usually prepared from the carbonate, which is found in nature and which is readily converted into other compounds by the action of acids. Moreover, in the preparation of potassium chloride from carnallite, magnesium chloride is

obtained as a by-product, and, since this is very soluble, it serves as a material for the preparation of the insoluble salts.

Magnesium Oxide (MgO); Magnesium Hydroxide ($Mg(OH)_2$) · Magnesium oxide can be prepared by any of the general methods for preparing oxides. Commercially it is obtained by heating the carbonate. It is a white powder, very soft and light. Commercially it is often known as *magnesia* or *magnesia usta*. With water it forms the hydroxide, but the combination takes place rather slowly. Because of its highly infusible character (melting point, 2800°), it is used in the manufacture of firebrick (as a lining for furnaces), for making crucibles, and for other purposes where a highly refractory substance is needed. It is used also for making flooring, and stucco and other cement building materials.

Magnesium hydroxide is but slightly soluble in water. When heated it is easily decomposed into the oxide and water. Magnesium salts, as a rule, are not toxic. Precipitated magnesium hydroxide is a white, insoluble, jellylike compound which acts as a mild alkali. Suspended in water (*milk of magnesia*), it is useful in neutralizing digestive acidity and as an antidote in acid poisoning.

Precipitation of Magnesium Hydioxide · Magnesium hydroxide, being insoluble, is precipitated when a solution of sodium or potassium hydroxide is added to a solution of a magnesium salt. With ammonium hydroxide, however, only a portion of the magnesium is precipitated. This is due to the fact that ammonium hydroxide is only slightly ionized, and in the presence of the ammonium salts formed in the reaction the extent of this ionization becomes still less, because of the influence of the ammonium ions present in the solution. As a result, the concentration of the hydroxyl ions becomes so small that the solubility product of magnesium hydroxide is no longer exceeded.

Magnesium Chloride ($MgCl_2 \cdot 6\ H_2O$) · Magnesium chloride is found abundantly in sea water, in salt brines, and in salt deposits. In the latter case it often occurs as the crystallized double chloride $KCl \cdot MgCl_2 \cdot 6\ H_2O$ (carnallite); and when potassium chloride is recovered from this salt, magnesium chloride becomes a by-product. From these natural sources (or by preparation from magnesite), magnesium chloride has become the compound from which nearly all magnesium is prepared. Mixed with calcium chloride, it is used to lay dust (p. 649). A floor plaster of magnesium oxide with a filler of fiber (wood or asbestos) moistened with magnesium chloride sets to a hard floor covering or cement consisting of the oxychloride, $3\ MgO \cdot MgCl_2 \cdot 10\ H_2O$. It is much improved in quality by the addition of 10 per cent of finely divided metallic copper.

Magnesium Metal from Sea Water · Magnesium metal is produced industrially, on a large scale, from the magnesium ions of sea water. In

the processing at Freeport, Texas, magnesium hydroxide is first precipitated from the sea water with lime, which has been made by burning oyster shells ($CaCO_3$, p. 649). To the precipitate, $Mg(OH)_2$, hydrochloric acid is added to convert it to magnesium chloride. This is then concentrated, dried, and fused; and finally, magnesium metal is deposited from the fused salt by electrolysis.

Magnesium Carbonate ***($MgCO_3$)*** · Magnesium carbonate occurs in a number of localities as *magnesite*, which is usually amorphous but sometimes forms crystals resembling calcite. More frequently magnesium carbonate is found associated with calcium carbonate. The mineral *dolomite* has the composition $CaCO_3 \cdot MgCO_3$. Limestone which contains smaller quantities of magnesium carbonate is known as *dolomitic limestone*. Dolomite is one of the most common rocks, forming whole mountain masses. It is harder and less readily attacked by acids than limestone. It is valuable as a building stone and for foundations, for lining certain types of furnaces, and as ballast for roadbeds. Magnesite is mined in California and Washington and used for making firebrick and other refractory material. Both magnesite and dolomite are the source material from which are prepared the corresponding oxides and hydroxides.

Magnesium carbonate readily dissolves in water containing carbon dioxide, forming the acid carbonate, which is often present in hard waters:

$$MgCO_3 + H_2O + CO_2 \longrightarrow Mg(HCO_3)_2$$

When a solution of a magnesium salt is precipitated with sodium carbonate, a white basic carbonate is obtained, known as *magnesia alba*, which is used as a cosmetic and as a medicine. As ordinarily prepared, its composition is expressed by the formula $3\ MgCO_3 \cdot Mg(OH)_2 \cdot 3\ H_2O$.

Magnesium Sulfate ***($MgSO_4$)*** · Like the chloride, this salt is to be found in many salt beds, and deposits of the nearly pure compound occur in Wyoming and Washington. Commercially, it is prepared from the chloride. A number of hydrates are known. The monohydrate occurs in the Stassfurt deposits as *kieserite*, but the form most commonly found is the heptahydrate, $MgSO_4 \cdot 7H_2O$, known as *Epsom salt*. This form is obtained by crystallizing magnesium sulfate from solution at ordinary temperatures, and, unlike kieserite, it is very soluble in water. All the hydrates yield the anhydrous salt when heated to 200°, and this in turn decomposes at a white heat, leaving a residue of magnesium oxide. Magnesium sulfate has many uses in the industries. It is used as a coating for cotton cloth, in the dyeing industry, in tanning, and in medicine.

Magnesium sulfate was the first magnesium compound to be described. In 1695 Grew, a London physician, called attention to its occurrence in the waters

of the famous spring located at Epsom, England; hence the name *Epsom salt.* It soon came into general use as a medicinal agent.

Magnesium Silicates · Many silicates containing magnesium are known, and some of them are important substances. *Serpentine, asbestos, talc* (or *soapstone*), and *meerschaum* are examples of such substances. Soapstone is a valuable material for making sinks and table tops. It is sometimes called *French chalk.* Asbestos is soft and fibrous and is a nonconductor of heat and of electricity. Because of its fibrous character it can be spun and woven into fabrics. It is used for fireproof material in a great variety of forms, such as paper, board, rope, and the fabric used for automobile brake-band linings. It is also used as a covering for pipes, furnaces, and boilers, to diminish heat radiation, and it has many uses as an insulator in electric devices. The chief source of asbestos is the province of Quebec, Canada. While the United States produces only about 2 per cent of the asbestos it uses, it nevertheless leads all other countries in the manufacture of asbestos products.

Other Magnesium Compounds · (1) *Magnesium sulfide* (MgS) is prepared by heating a mixture of magnesium and sulfur. It is a yellowish-gray solid and resembles calcium sulfide in its action toward water. (2) *Magnesium nitride* (Mg_3N_2) is formed by the direct union of magnesium and nitrogen at high temperatures. It reacts with water, forming magnesium hydroxide and ammonia. (3) *Magnesium citrate* (the magnesium salt of citric acid) is a common medicinal. (4) The *phosphates of magnesium* resemble those of calcium in their composition and general properties. When a solution of disodium phosphate is added to a solution of any magnesium compound containing ammonium hydroxide, magnesium ammonium phosphate is precipitated:

$$MgSO_4 + Na_2HPO_4 + NH_4OH \longrightarrow MgNH_4PO_4\downarrow + Na_2SO_4 + H_2O$$

This crystallizes in the form of the hexahydrate, which is somewhat unstable. If filtered off and heated to redness, however, it is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), which is perfectly stable:

$$2\,MgNH_4PO_4 \longrightarrow Mg_2P_2O_7 + 2\,NH_3\uparrow + H_2O\uparrow$$

From the weight of the pyrophosphate it is possible to calculate the weight of magnesium present in the original solution. These reactions serve in the laboratory for the quantitative determination either of magnesium or of phosphoric acid.

Calcium and Its Compounds

The Metal · Davy first isolated calcium by the electrolysis of the hydroxide. It is now prepared by the electrolysis of the melted chloride,

and a number of different cells have been devised for effecting the electrolysis (p. 639).

Calcium is a silvery, white metal, but acquires a slightly yellowish tinge upon exposure to air, owing to its union with nitrogen. It combines readily with most of the nonmetals, often with the evolution of light. When heated to ignition in oxygen, it burns with dazzling brilliancy. When it is burned in air, both its oxide and its nitride are obtained. It combines directly with hydrogen to form the hydride, CaH_2. It reacts with water and with dilute acids, as represented in the following equations:

$$Ca + 2\ H_2O \longrightarrow Ca(OH)_2 + H_2\uparrow$$
$$Ca + H_2SO_4 \longrightarrow CaSO_4 + H_2\uparrow$$

Calcium promises to become a useful metal, although its commercial applications are as yet rather limited. It is a powerful reducing agent and would undoubtedly find application in the reduction of some of the metallic oxides if it could be produced at a sufficiently low cost.

Compounds of Calcium · Compounds of calcium are found in large quantities in various regions. The most abundant of these compounds is the carbonate, which occurs in many different forms, such as *marble* and *limestone*. Other calcium-bearing minerals are listed in the table on page 638.

The preparation of the compounds of calcium does not in general present as great a problem as does the preparation of those of sodium (p. 291). This is due to the fact that the form in which calcium occurs most abundantly in nature is its carbonate, a compound which is readily changed into other compounds by the action of the appropriate acids. Moreover, the carbonate can be decomposed by heat without difficulty, which furnishes an inexpensive method for the preparation of the oxide (lime).

Calcium Oxide (Lime) (CaO) · Calcium oxide, known also as *lime*, *quicklime*, and *burnt lime*, may be obtained by burning the metal in air or by heating the nitrate or carbonate. It is obtained commercially by heating limestone in large furnaces:

$$CaCO_3 \rightleftarrows CaO + CO_2\uparrow$$

The reaction is reversible, as is indicated in the equation. If the decomposition is carried out in a closed vessel, equilibrium between the opposing reactions is reached at any definite temperature when the dissociation pressure reaches a definite value characteristic of that temperature (p. 446). The higher the temperature, the greater the pressure at equilibrium.

If, on the other hand, the carbon dioxide is conducted away as fast as formed, the decomposition will continue until complete. This is the method adopted in

the production of lime, the limestone being heated in a current of air, which carries away the carbon dioxide.

Pure calcium oxide is a white amorphous substance whose density is about 3.4. When heated intensely, as in the oxyhydrogen blowtorch, it gives a brilliant light. It has a high melting point, namely 2572°, and boils vigorously (2850°) when heated in an electric furnace. It acts upon water, with the evolution of considerable heat (whence the name *quicklime*, or "live lime"), the process being called *slaking*. The equation is

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 16{,}100 \text{ cal}$$

Because of its affinity for water it is used for drying gases. It also absorbs carbon dioxide, forming the carbonate:

$$CaO + CO_2 \longrightarrow CaCO_3$$

Lime exposed to air is therefore gradually converted into the hydroxide and the carbonate and will no longer slake with water. It is then said to be *air-slaked*. Lime is produced in nearly every state, Ohio and Pennsylvania leading in the production. Its greatest use is in the preparation of calcium hydroxide, largely employed in building construction. It has many other uses, as in the production of wood pulp and paper, and in the manufacture of glass, and of calcium carbide, from which acetylene is prepared.

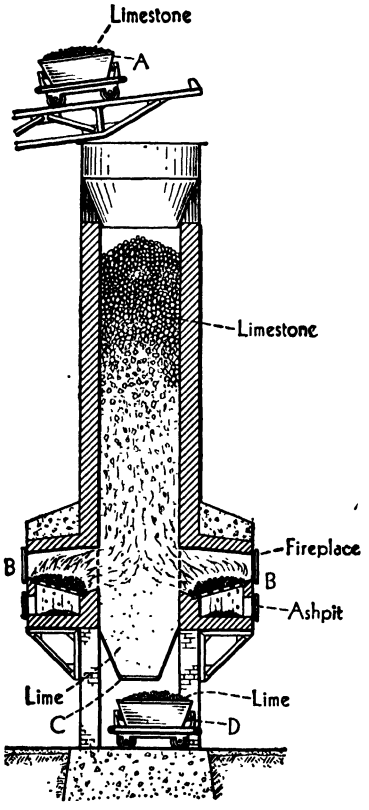


Fig. 36-3. A Vertical Section of a Limekiln

Calcium carbonate, on being heated, decomposes less readily than does magnesium carbonate; and calcium oxide reacts more vigorously with water than does magnesium oxide, and with the evolution of more heat.

Commercial production of lime. Lime is made by heating limestone in large, chimney-like furnaces called *limekilns*. A vertical section of a modern limekiln is shown in Fig. 36-3. The kiln is about 50 ft in height. The fireboxes, or furnaces (*B*, *B*), are built around the lower part, and lead into the central stack. Limestone is added at the top of the kiln, as shown at *A*. The hot gaseous products of combustion are drawn up through the kiln, and the limestone is gradually decomposed by the

heat. The bottom of the furnace is so constructed that a current of air is drawn in at *C*. This serves the purpose of cooling the hot lime at the base of the furnace, of furnishing heated oxygen for the combustion, and of removing the carbon dioxide from the kiln. The lime is dropped into cars, *D*, run under the furnace. Usually several of these kilns are operated together.

Calcium Hydroxide (Slaked Lime) **($Ca(OH)_2$)** · This important compound results when lime is treated with water:

$$CaO + H_2O \rightleftarrows Ca(OH)_2$$

The reaction is reversible, and the oxide can be obtained from the hydroxide by heating the latter above 450° in an open vessel. Calcium hydroxide is usually a white powder, though under proper conditions it can be crystallized from water in glittering crystals of the formula $Ca(OH)_2 \cdot H_2O$. It is very sparingly soluble in water, and its solubility diminishes with rise in temperature. At 10°, 1 liter of water dissolves 1.76 g of the hydroxide; at 50°, 1.28 g; and at 100°, only 0.77 g.

Its solution in water is called *limewater* and is often used in medicine because of its basic properties. Because of its low cost calcium hydroxide is much used in the industries whenever a mild alkali is desired. It has a wide variety of uses, the most important of which are as follows: in the manufacture of various building materials, such as mortar, plaster, stucco, and like products; in the softening of water; in the manufacture of insecticides, such as the lime-sulfur sprays (p. 782); in the preparation of bleaching powder and of the hydroxides of sodium and potassium; for agricultural purposes, especially for neutralizing the acid in sour soils; in purifying coal gas; and in removing the hair from hides in the manufacture of leather.

Mortar; Plaster; Stucco · Ordinary mortar consists of a mixture of calcium hydroxide, sand, and water. When exposed to air, the water is absorbed or evaporates, and the mortar gradually hardens, or sets. In this process the calcium hydroxide is slowly acted upon by the carbon dioxide in the air, forming calcium carbonate. At present cement enters largely into the composition of mortars.

Formerly, the plaster applied to interior walls of buildings consisted of a mixture of calcium hydroxide and hair or wood fiber. At present various manufactured products are used in which plaster of Paris is the principal constituent. Plasters applied to the exterior of buildings are called *stucco*. They consist of sand or other filler together with a binding material. Formerly the binder was always a paste of lime, though in modern practice cement is generally mixed with the lime. Colored sand or added coloring materials afford a wide range of color, and the coating is very durable if the understructure is good.

Lime-stucco plasters have been used from the earliest days, dating back to Mesopotamia in 3500 B.C. They were much used by Egyptians, Greeks, Romans, and Moors in their best periods of architecture. In 1505 Raphael examined the Golden House of Nero and as a result revived the use of hard stucco in Italy. Thence its use spread widely into most European countries, and many of their finest architectural monuments are stucco-covered.

Calcium Fluoride **(CaF_2)** · This salt occurs in large quantities in nature as *fluorite*. The mineral crystallizes in the form of cubes or octahedra, and large crystals are often found that are beautifully colored, usually a shade of green or blue. When heated gently, they become fluorescent. Calcium fluoride occurs also in the ashes of some plants. It is an essential constituent of the enamel of teeth. When pure it is a white solid and is nearly insoluble in water. It melts at 1360°. The mineral fluorite is mined principally in southern Illinois and Kentucky. Its chief use is as a flux in the manufacture of steel. It is used also in the manufacture of opaque glass and white enamel, and in the preparation of hydrofluoric acid.

Calcium Chloride **($CaCl_2$)** · This salt is present in sea water in small percentages. It is formed in large quantities as a by-product in the manufacture of a number of compounds, and especially of sodium carbonate by the Solvay process (p. 294). The natural brines from which salt and bromine are obtained also constitute a large source of calcium chloride. Pure calcium chloride may be prepared by dissolving calcium carbonate in hydrochloric acid and evaporating the resulting solution to crystallization. It separates from saturated solutions at ordinary temperatures in the form of hexagonal crystals, which have the formula $CaCl_2 \cdot 6\,H_2O$. The mono-, di-, and tetra- hydrates have also been prepared. When the hydrates are heated above 260°, the anhydrous salt is obtained as a white porous mass. In this process some calcium oxide is formed by the action of water upon the chloride:

$$CaCl_2 + H_2O \longrightarrow CaO + 2\,HCl$$

As a rule, therefore, a solution of the anhydrous salt reacts basic, owing to the presence of calcium hydroxide.

The anhydrous salt readily absorbs moisture and is largely used as a drying agent (p. 94). It dissolves in water, with the liberation of considerable heat, while the hexahydrate absorbs heat when it dissolves. Calcium chloride is very soluble, 100 g of water dissolving 42.7 g at 20°. Owing to its great solubility, the boiling point of a concentrated solution of calcium chloride is much higher than that of water. The solid hexahydrate and ice form a freezing mixture by means

of which a temperature as low as — 54.9° can be reached (p. 202). A solution of calcium chloride is largely used as a brine in the manufacture of artificial ice. Because of its deliquescent character it has been used to lay the dust on roads to free coal from dust, and to prevent newly laid concrete from drying too rapidly. Mines have also been sprinkled with its solution in the hope of preventing dust explosions (p. 594).

Calcium Carbonate ***($CaCO_3$)*** · Enormous quantities of calcium carbonate occur in nature. *Limestone* is the most abundant form. It is a grayish rock that is usually found in hard, stratified masses. Whole mountain ranges are sometimes made up of this material. It is never pure calcium carbonate, always containing variable percentages of foreign matter, usually magnesium carbonate, clay, silica, compounds of iron and aluminum, and frequently fossil remains. *Marl* is a mixture of limestone and clay. *Pearls*, *coral*, various kinds of *shells* (such as eggshells and oyster shells), and *natural chalk* (not the blackboard crayon) are largely calcium carbonate.

Calcium carbonate is a dimorphous substance. (1) The more common form of crystal belongs to the hexagonal system. *Calcite* is a pure, crystalline form of this character. Very beautiful transparent crystals of calcite are found in Iceland; hence the name *Iceland spar*, often applied to this variety. *Mexican onyx* is a massive variety, streaked or banded with colors occasioned by impurities. *Marble* is made up of minute, snow-white calcite crystals, and was probably formed by the crystallization of the melted rock under great pressure. *Stalactites* and *stalagmites* are icicle-like forms, sometimes found in caves. (2) Calcium carbonate is also found in nature in the form of crystals belonging to the rhombic system. The mineral *aragonite* is an example of this form. When heated, it is transformed into a mass of calcite crystals. This transformation probably takes place at ordinary temperatures. It is easy to understand, therefore, why the aragonite form is a rather uncommon variety, even though the transformation is slow.

Production and Uses of Limestone · Limestone is mined in all but three or four of the states (nearly 100,000,000 tons annually); Ohio, Pennsylvania, New York, and Michigan, in the order named, lead in its production. More than half of the amount mined is crushed and used in the construction of roads and in making concrete. It is our principal building stone. Large amounts are utilized as a flux in separating metals from their ores, and, in powdered form, for neutralizing the acid present in certain soils. It is the source of all commercial lime and, in addition, has numerous minor uses.

Preparation of Pure Calcium Carbonate · In the laboratory pure calcium carbonate can be prepared by precipitation:

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2\,NaCl$$

When the precipitation is effected at ordinary temperatures, the carbonate is obtained as an amorphous powder, which soon changes over into calcite crystals. When the carbonate is precipitated from hot dilute solutions, aragonite crystals are obtained, but these slowly change into the calcite form.

Pure calcium carbonate is very slightly soluble in water, 1 liter of water at 15° dissolving but 13 mg, or, if it is in the form of aragonite, 15 mg. The action of acids upon this substance, as well as the effect of heat upon it, has already been discussed.

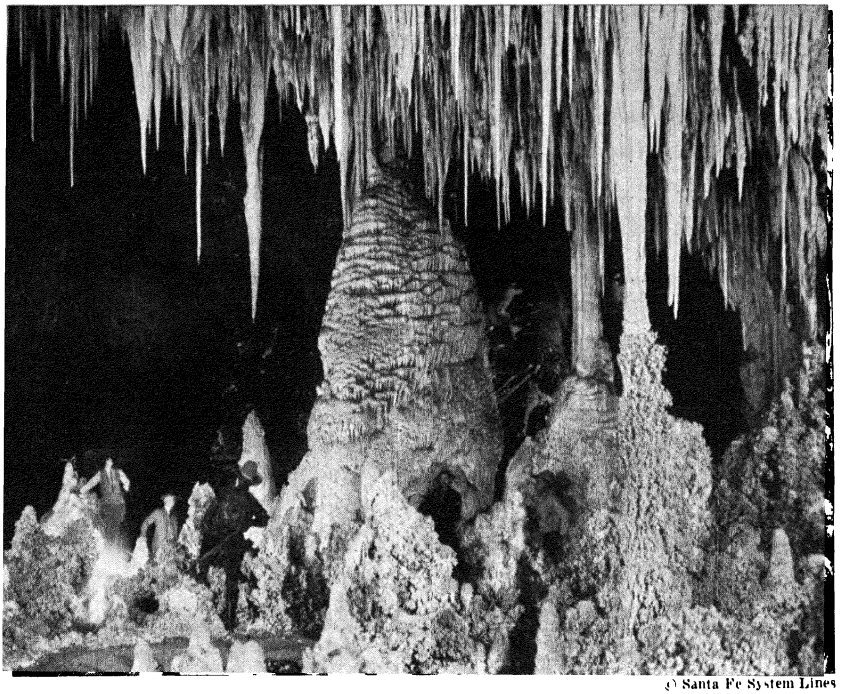
Calcium Acid Carbonate (Calcium Bicarbonate) ($Ca(HCO_3)_2$) · While calcium carbonate is almost insoluble in pure water, it readily dissolves in water containing carbon dioxide. This is due to the formation of the soluble but unstable calcium acid carbonate. When solutions containing the acid carbonate are heated, the normal carbonate is precipitated:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

Natural waters always contain more or less carbon dioxide in solution. In the case of certain underground waters the amount of carbon dioxide is comparatively large, since it is held in solution by pressure. Such waters have a marked solvent action upon limestone, dissolving both the calcium carbonate and the magnesium carbonate. In certain localities this solvent action, continued through geological ages, has resulted in the formation of large caves in limestone rock, such as the Mammoth Cave in Kentucky. Water containing calcium bicarbonate, seeping from the roof of such caves and evaporating, deposits calcium carbonate, often in the form of stalactites and stalagmites (Fig. 36-4).

Calcium Sulfate ($CaSO_4$) · This compound occurs in nature in the anhydrous form in the mineral *anhydrite*. More commonly, however, it is found as *gypsum*, which is a dihydrate ($CaSO_4 \cdot 2\,H_2O$). Several other varieties of calcium sulfate are known, such as *selenite*, *alabaster*, and *satin spar*. Calcium sulfate is but slightly soluble in water; its solubility increases slowly from 0° to about 35°, and then decreases at higher temperatures.

Of the different forms of calcium sulfate, gypsum is by far the most important. Our supply comes chiefly from New York, Michigan, Iowa, and Texas, although it is mined in a number of other states; considerable amounts are also imported from Canada. It crystallizes in a prismatic form belonging to the monoclinic system. Its principal use is in making



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Fig. 36-4. View in the Carlsbad Caverns (New Mexico), Showing Stalactites and Stalagmites

plaster of Paris. Large quantities are also utilized in making cements (see Portland cement, p. 767), as a filler for paper, as a paint pigment, and as a constituent of fertilizers. Its value as a fertilizer seems to be due to the fact that it reacts with the ammonium carbonate present in soils, forming ammonium sulfate, which is much less volatile than the carbonate and is therefore retained in the soil until absorbed by the growing plant.

Plaster of Paris · This is a fine white powder obtained by carefully heating gypsum to about 125°; it consists essentially of the hydrate, $(CaSO_4)_2 \cdot H_2O$. When water is added, this powder forms a plastic mass, which quickly hardens, or sets, expanding slightly in the process, and regains the crystalline structure of gypsum. These properties make it valuable for casts and stucco work, for cementing glass to metals, and for a finishing coat on plastered walls. When mixed with wood pulp (or a similar product) and allowed to set in flat sheets, it forms a material much used in the construction of buildings, especially in place of plaster.

Sulfites of Calcium · The normal sulfite, $CaSO_3$, being but slightly soluble, is formed as a white precipitate when a solution of sodium sulfite

is added to a solution of a calcium salt. When it is suspended in water and treated with sulfur dioxide, it dissolves, owing to the formation of the soluble bisulfite, $Ca(HSO_3)_2$. A solution of this salt with some free sulfurous acid is used in large quantities in the manufacture of paper (p. 545). Two methods are used for its preparation on a large scale:

1. Sulfur dioxide is passed into a solution of calcium hydroxide:

$$Ca(OH)_2 + 2\ H_2SO_3 \longrightarrow Ca(HSO_3)_2 + 2\ H_2O$$

2. Sulfur dioxide is passed upward through large towers filled with limestone, over which water trickles:

$$CaCO_3 + 2\ H_2SO_3 \longrightarrow Ca(HSO_3)_2 + H_2O + CO_2\uparrow$$

Calcium Carbide (CaC_2) · This compound is now prepared on a large scale for use in generating acetylene (p. 519) and in making fertilizer. It is made by heating a mixture of coke and lime in an electric furnace:

$$CaO + 3\ C \longrightarrow CaC_2 + CO\uparrow$$

Plants for its manufacture are located at places like Niagara Falls, Keokuk (Iowa), and Muscle Shoals (Alabama), where water power is utilized in generating the necessary electric current for operating the furnaces.

The pure carbide is a colorless, transparent, crystalline substance and is practically insoluble in all known solvents. The commercial article is a dull-gray porous substance which contains many impurities. At high temperatures it is a powerful reducing agent. Its commercial importance lies in the fact that it easily reacts with water to form *acetylene* and with nitrogen to form calcium *cyanamide* ($CaCN_2$)—a valuable material in the manufacture of fertilizers.

Commercial Production of Calcium Carbide · The general form of furnace used for making calcium carbide on a large scale is shown in Fig. 36-5. The sides and bottom of the furnace are built of brick, and large carbon electrodes, *A*, extend into the furnace. The furnace is nearly filled with a mixture of coke and lime, *B*. The current is then connected and regulated so as to secure a temperature of about 2000°. At this temperature the carbide gradually forms. As the temperature is above its melt-

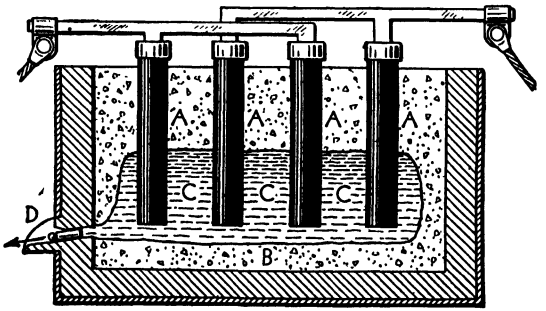


Fig. 36-5. A Furnace for the Production of Calcium Carbide

ing point, it separates in liquid form, *C*, and is drawn off at the outlet, *D*. The process is continuous, raw materials being added from time to time as the carbide is withdrawn. These furnaces are really large brick rooms.

***Calcium Cyanamide* ($CaCN_2$)** · This compound is formed when nitrogen is passed over calcium carbide heated to about 1200°:

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

The compound is a derivative of *cyanamide* ($H_2N—C{\equiv}N$, or H_2CN_2), the two hydrogen atoms of the cyanamide being replaced by the bivalent calcium atom. The commercial product, known as *lime nitrogen*, contains about 60 per cent of cyanamide; the remaining 40 per cent consists chiefly of carbon and lime. This is ground and mixed with water (which slakes the lime) and in this form is sold as a fertilizer under the name *cyanamide*. Its value as a fertilizer lies in the fact that all its nitrogen is available as a plant food.

Calcium cyanamide is of importance in the commercial preparation of ammonia and sodium cyanide. The ammonia is obtained by treating the cyanamide with steam, while the cyanide results from the action of sodium chloride. The equations for the reactions are as follows:

$$CaCN_2 + 3\,H_2O \longrightarrow CaCO_3 + 2\,NH_3\uparrow$$
$$CaCN_2 + C + 2\,NaCl \longrightarrow CaCl_2 + 2\,NaCN$$

The nitrogen used in the preparation of the cyanamide is obtained from liquid air (p. 103). By means of the reactions above it is possible, therefore, to convert the nitrogen of the air into important compounds of nitrogen.

Phosphates of Calcium · With phosphoric acid, calcium forms three salts, the names and formulas of which are as follows:

Tricalcium phosphate	$Ca_3(PO_4)_2$
Calcium monohydrogen phosphate	$CaHPO_4$
Calcium dihydrogen phosphate	$Ca(H_2PO_4)_2$

The occurrence, mining, and uses of tricalcium phosphate have been given in connection with the description of the compounds of phosphorus (p. 414). The pure salt can be obtained by adding ammonium hydroxide to a solution of a calcium salt until strongly alkaline, and then precipitating with disodium phosphate:

$$3\,CaCl_2 + 2\,NH_4OH + 2\,Na_2HPO_4 \longrightarrow Ca_3(PO_4)_2\downarrow + 4\,NaCl + 2\,NH_4Cl + 2\,H_2O$$

It is nearly insoluble in water but easily dissolves in acids, even in very weak ones like acetic acid.

Calcium dihydrogen phosphate is deposited in the form of white crystals when a solution of tricalcium phosphate in phosphoric acid is evaporated:

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \longrightarrow 3\ Ca(H_2PO_4)_2$$

When a solution of disodium phosphate is added to a solution of a calcium salt, calcium monohydrogen phosphate is obtained:

$$CaCl_2 + Na_2HPO_4 \longrightarrow CaHPO_4 + 2\ NaCl$$

Both the acid salts are also formed, along with calcium sulfate, by the action of sulfuric acid upon tricalcium phosphate (p. 418).

Strontium and Its Compounds

Occurrence and Preparation · Although somewhat widely distributed, strontium is the least abundant of the alkaline-earth metals. Its chief minerals are *celestite* ($SrSO_4$) and *strontianite* ($SrCO_3$). At Put in Bay (Ohio) beautiful large crystals of celestite are found lining the walls of Strontia Cave. The largest deposits of the strontium ores in the United States are in Arizona, Texas, and Utah. At the present time, however, we obtain almost our entire supply from England.

The preparation of strontium is much more difficult than that of calcium, although the general methods involved are the same. It is expensive and has no commercial uses. The compounds of strontium are very similar to those of calcium and are of much less importance; so they will be described very briefly.

Strontium Oxide **(SrO)**; ***Strontium Hydroxide*** **($Sr(OH)_2$)** · The oxide is obtained by heating the carbonate. It combines with water to form the hydroxide, which is a moderately strong base. The latter is fairly soluble in hot water, and crystallizes from the solution in the form of the octahydrate, $Sr(OH)_2 \cdot 8\ H_2O$. The hydroxide forms with sucrose an insoluble compound which can easily be decomposed into its original components. It was formerly used in the United States for the refining of sugar—to extract the sugar from uncrystallizable sirups—and is still used for this purpose in European countries.

Strontium Nitrate **($Sr(NO_3)_2$)** · From a hot aqueous solution this salt separates in the anhydrous form, while from a cold solution it separates as a tetrahydrate, $Sr(NO_3)_2 \cdot 4\ H_2O$. When ignited with combustible materials, it imparts a brilliant crimson color to the flame and is therefore used in the manufacture of red lights. It is also used in making flares and signal lights.

Other Compounds of Strontium · Among the other compounds of strontium the following may be mentioned: *strontium chloride* ($SrCl_2 \cdot 6\ H_2O$), *strontium*

bromide ($SrBr_2$), and *strontium iodide* (SrI_2), which are all white solids, very soluble in water; *strontium sulfide* (SrS); *strontium carbonate* ($SrCO_3$), prepared from the chloride or nitrate by precipitation with ammonium carbonate. A number of compounds of strontium are used in medicine.

Barium and Its Compounds

Occurrence · Like strontium and calcium, barium is widely distributed as a constituent of igneous rocks, although present in small percentages only. Its most abundant forms are the minerals *barite* ($BaSO_4$) and *witherite* ($BaCO_3$). The former is the more abundant and is the mineral from which the other compounds of barium are prepared.

Preparation and Uses · Barium is prepared by the same general process used in the preparation of calcium and strontium, and it resembles these metals in its properties. Probably because of its cost there has been little demand for the metal. In late years the demand has increased, owing to the use of the metal in the manufacture of radio tubes and to harden lead for bearing alloys.

Compounds of Barium · The compounds of barium are very similar to those of calcium and strontium. They are prepared either directly or indirectly from barite. This is first converted into the sulfide or carbonate, and from these the chloride and nitrate are prepared by the action of the appropriate acids. The soluble compounds of barium are poisonous.

Oxides of Barium; Barium Hydroxide · Barium oxide (BaO) can be obtained by strongly heating the nitrate:

$$2\ Ba(NO_3)_2 \longrightarrow 2\ BaO + 4\ NO_2\uparrow + O_2\uparrow$$

When heated to a low red heat in the air, the oxide combines with oxygen, forming the peroxide, BaO_2, which is used in making hydrogen peroxide (p. 96). Barium oxide readily combines with water to form the hydroxide, $Ba(OH)_2$, a white solid which is more soluble in water than calcium hydroxide.

Barium Chloride ($BaCl_2$) · Barium chloride is a white solid, and from its solution it crystallizes as the hydrate, $BaCl_2 \cdot 2\ H_2O$. It is used in the laboratory as a reagent to detect the presence of sulfuric acid or soluble sulfates, since it reacts with these to form insoluble barium sulfate.

Barium Sulfate ($BaSO_4$) · This compound is by far the most widely used of the compounds of barium. With the exception of the sulfate of the rare metal radium, it is the least soluble of all the sulfates, and is precipitated, even in the presence of strong acids, when sulfuric acid or a solution of any sulfate is added to a solution of a barium salt. The native barium sulfate is a heavy mineral; hence the name *barite* (from a

Greek word meaning "heavy"), from which the name of the metal itself was derived. Large quantities of barite are mined in the United States (especially in Missouri), and more than half of the production is used in the manufacture of paint pigments, chiefly *lithopone* (a mixture of barium sulfate and zinc sulfide); the remainder is used in the preparation of other compounds of barium and in the manufacture of procelains for spark plugs.

Other compounds of barium. *Barium carbonate* ($BaCO_3$) is sometimes mixed with clay in the manufacture of terra-cotta ware. *Barium nitrate* ($Ba(NO_3)_2$) is an oxidizing agent, and combustible materials mixed with it burn with a green flame. It is therefore used in the manufacture of green lights. *Barium sulfide* (BaS) resembles the sulfides of calcium and strontium; it hyrolyzes with water, forming the hydroxide and acid sulfide. *Barium chromate* ($BaCrO_4$) is a yellow solid insoluble in water.

Radium

Radium occurs only in uranium minerals, and practically all our supply comes from pitchblende (U_3O_8), of which there are rich deposits in the Belgian Congo and in the Great Bear Lake region of Canada. Only 1 g of radium is present in 3.88 tons of the purest pitchblende. Since the ores used are never pure, the yield of radium per ton is actually much less than that noted above. About 100 g of radium is prepared annually.

Radium behaves chemically like barium, and forms a chloride, $RaCl_2$; a bromide, $RaBr_2$; a sulfide, RaS; and a sulfate, $RaSO_4$.

The chief interest in radium is in its radioactivity, which, being a property of the atomic nucleus (p. 321), is shown by the salts as well as by the free element. The very penetrating gamma rays are effective in the treatment of cancer, and large hospitals are supplied with small amounts. It is kept in lead "bombs," the walls of which are about 4 in. thick, to prevent the dangerous rays from passing through the metal. Usually, instead of using radium itself or its compounds, the gas radon, given off by nuclear decomposition of radium, is collected and sealed into small, thin-walled glass ampules, "needles," or "seeds." Gold "seeds," or tiny gold capillary tubes, are also used to hold the radon. These are then inserted into the cancerous tissue, which is "killed" by the gamma rays. Other cancer treatments include the use of high-intensity X rays and of the radiations from radioactive cobalt and gold prepared in atomic reactors (p. 805).

In the industries minute quantities of a mixture of radium compounds and mesothorium (an isotope of radium) are worked into varnishes and

enamels and applied to watch hands, electric pushbuttons, and the like to render them visible in the dark.

QUESTIONS

1. How can you account for the validity of the following statements about the elements of Group IIA?

a. The hydroxides of calcium, strontium, and barium should be strong bases.

b. Beryllium hydroxide can be expected to be less basic than the hydroxides of the other elements of this group.

c. All the elements of this group should show an electrovalence of + 2.

d. Barium and strontium metals may be expected to be soft and malleable.

e. The properties of calcium, strontium, and barium should be more nearly alike than those of beryllium, magnesium, and calcium.

f. The solubilities of the salts of this group might be expected to be considerably different from those of the elements of the alkali family.

g. The properties of radium should be similar to those of barium.

2. Give a simple method for distinguishing between the following pairs: (*a*) potassium carbonate and strontianite; (*b*) fluorite and barite; (*c*) gypsum and wollastonite; (*d*) potassium chloride and barium chloride; (*e*) calcite and witherite.

3. Metallic calcium reacts readily with water. Would this prevent its use in alloys?

4. Lime is produced in very large quantities; yet its uses appear to be limited. What is the explanation?

5. For what purposes are (*a*) calcium bisulfite and (*b*) calcium sulfate used in making paper? (*c*) Would these uses be predicted on chemical grounds?

6. If strontium and barium were as abundant as calcium, can you suggest any present uses of calcium that would be replaced by compounds of these two elements?

7. Ammonium hydroxide will not precipitate magnesium hydroxide from a solution containing magnesium ions and ammonium ions. Explain why this is true.

8. Barium sulfate is but slowly changed by a solution of sodium carbonate, while in a *fusion* of that salt the change into barium carbonate is very rapid. Why?

9. Calcium fluoride is at once precipitated when calcium ions and fluorine ions are brought together in solution, whereas the equally insoluble calcium oxalate is not precipitated by the action of a solution of a calcium salt with oxalic acid. Why?

10. (*a*) In what way does the equilibrium between calcite and aragonite compare with that between the two forms of sulfur? (*b*) How does it compare with that between graphite and diamond?

11. How is soil "sweetened" by adding lime?

12. What salts of beryllium, magnesium, and calcium should you expect would hydrolyze? Why?

13. In what ways is magnesium more similar to calcium than to zinc?

14. How would you prepare barium sulfate ($BaSO_4$) from barium chloride ($BaCl_2$), and vice versa?

PROBLEMS

1. (*a*) What is the molar concentration of a saturated solution of calcium hydroxide at 10°? (*b*) Assuming 90 per cent ionization, give the gram-ion concentration of Ca^{++} and of OH^-.

2. A limekiln uses 50 tons of limestone daily. Assume the formula weight of calcium carbonate to be 100, and the material to be 90 per cent pure. (*a*) Without use of atomic weights, calculate the volume of carbon dioxide, under standard conditions, that will be evolved. (*b*) What weight of Dry Ice will this make if we assume no loss of the carbon dioxide?

3. What weight plaster cast can be made from 100 kg of plaster of Paris?

4. A firm has available daily 1000 kg of pyrite (FeS_2) for the manufacture of calcium bisulfite to be used in a paper mill. From this source of sulfur, what weight of calcium bisulfite can be furnished daily?

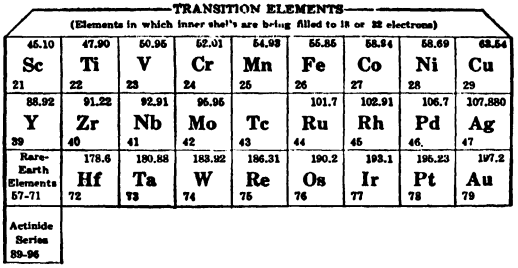
5. What percentage of Epsom salt consists of water of hydration?

6. (*a*) Calculate the $[Mg^{++}]$ in a saturated solution of magnesium hydroxide at 25° if the value of the solubility-product constant (K_{sp}) of magnesium hydroxide is 3.2×10^{-11}. (*b*) Calculate the grams of magnesium hydroxide dissolved in 1000 g of water at that temperature.

CHAPTER 37

TRANSITION ELEMENTS: ATOMS WITH UNFILLED SUBSHELLS

Some of our most important metals are those that belong to a group known as transition elements. The atoms of this group of elements are characterized by unfilled inner shells of electrons—shells which can hold 18 or 32 electrons (see Appendix). Several of the chemical properties,



Transition Elements in Which an Electron Shell of 8 Is Being Filled to 18 or 32

such as color, complex formation, and oxidation states of these elements can be explained in terms of the unfilled inner shells.

It is our purpose here to study the properties and chemical behavior of the transition elements and to try to correlate these properties with the structure of the atoms of these elements.

Subshells and Orbitals · The transition elements can react in two ways, (1) by losing electrons, thus producing positive ions, which in turn (2) may share electrons in the unfilled shell, thereby forming complex ions. In order to understand this second type of compound we must first learn something about how the electrons in the atoms are arranged and how they can be used to form chemical bonds.

We have learned that the electrons of an atom are located in shells and subshells (p. 333). For example, the main electron shells, called K, L, M, N, are really made up of the following subshells, with the indicated total number of electrons in each sublevel.

Main shell	1 or K	2 or L	3 or M	4 or N
Subshells	s	s, p	s, p, d	s, p, d, f
Number of electrons in each subshell	2	2, 6	2, 6, 10	2, 6, 10, 14

We frequently assign the numbers 1, 2, 3, 4 instead of capital letters to the main shell, and indicate the number of electrons in each subshell by a superscript. Hence $1s^2$, $2s^2$, and $3s^2$ indicate two s electrons in each of the main shells 1, 2, 3 (or K, L, M); while $2p^6$, $3d^{10}$ indicate six electrons in the p level of the second main shell (L shell) and ten electrons in the d level of the third main shell (M shell).

The electrons in these subshells tend to pair off as a result of opposite spins of the electrons, and a bond seems to be formed between the pair. We sometimes represent this condition of pairing electrons in sublevels by circles containing a pair of electrons. Hence we can show the electrons in a neon atom, which has 10 electrons, in the manner of Fig. 37-1. These paired electrons (or possible places to put a pair of electrons) in each subshell are commonly referred to as *orbitals*. Thus the s electrons in each subshell have or form one orbital, the p electrons have 3 orbitals, the d electrons 5 orbitals, and f electrons 7 orbitals. Fig. 37-2 indicates the orbitals in each level.

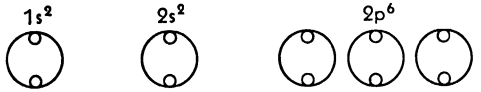


Fig. 37-1. Orbitals of a Neon Atom

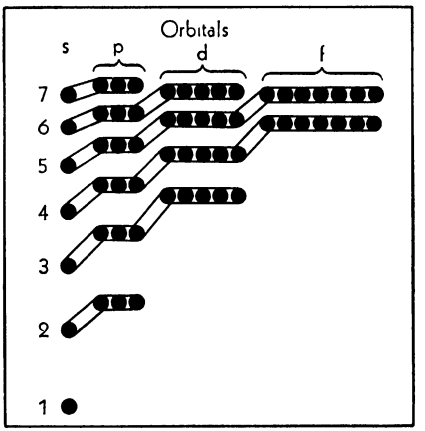


Fig. 37-2. Orbital Levels · This diagram shows the relative energy levels of the different orbitals in atoms

If there is an insufficient number of electrons in an atom to fill all orbitals with pairs, then the electrons arrange themselves with one electron per orbital. Only after each orbital has one electron do the electrons begin to pair off.

For example, consider the orbitals in the nitrogen atom, in which seven electrons may be represented as in Fig. 37-3.

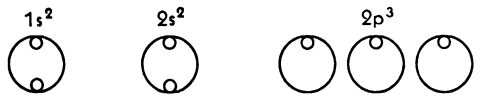


Fig. 37-3. Orbitals of a Nitrogen Atom

Relative Energy Levels of the Subshells · Now our problem becomes somewhat complicated as we trace the relative values of the energy levels of the subshells. You will recall that on page 333 the following order of the energy levels was revealed:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p, \text{ etc.}$$

(where < means "less than"). This is shown in Fig. 37-2. It will be noticed that all the orbitals of the L shell (the $2s$ and $2p$ orbitals) are higher energy levels than the $1s$ orbital in the K shell; that all the orbitals in the M shell (the $3s$, $3p$, and $3d$ orbitals) are of higher energy than those in the L shell; but that the $4s$ orbital in the N shell has a lower energy level than the $3d$ orbitals in the M shell. Consequently, as we progress along the series of elements arranged according to the order of increasing atomic number, we find that after the two $4s$ electrons of the N shell have been assigned their places (the elements potassium and calcium) the succeeding elements will add their additional electrons in the $3d$ orbitals of the underlying shell until these are filled. This gives rise to a series of ten elements which have two electrons only in the outer shell. These elements are called "transition" elements. A second such series will be found following strontium. A third series follows barium, in which there are fifteen elements (the rare earths, or lanthanides), whose atoms differ only in the number of electrons in the $4f$ orbitals in the N shell, which is the second inner shell. These fifteen elements are then followed by ten which differ only in the electrons in the d orbitals of the O shell, the first inner shell.

Properties of the Transition Elements · Because the transition elements do not differ in the number of electrons in the valence shell, but only in the number of electrons in underlying shells, they show many points of similarity, both as the free metals and in their compounds. This is particularly true when we compare the elements in corresponding oxidation states. Thus the compounds of bivalent manganese, iron, cobalt, nickel, and copper have many points of similarity. In fact, in many respects the similarity in a horizontal row, or long period, of the periodic table is more marked in the long periods containing the transition elements than are the relationships in the vertical row, or family. Nickel, for example, is, in most of its chemical properties, more like cobalt and copper than it is like palladium and platinum. There are three characteristics of the transition elements which distinguish them as a class. They are characterized (1) by variable oxidation states (valence), (2) by the fact that they form stable complex ions, and (3) by the fact that their salts are nearly always colored.

1. **Variable oxidation states.** As one might expect, the two s electrons of the valence shell of the atoms of the transition elements are available for chemical reactions, and most of the transition elements are found in an oxidation state of $+2$. Thus we find such compounds as $MnSO_4$, $FeCl_2$, $Co(NO_3)_2$, and $CuCO_3$. The underlying d electrons, however, are not greatly different in energy from the two s electrons, and under suit-

able conditions they, too, may act as valence electrons, so that the transition elements show a great variety of oxidation states. The most important of these are shown in the adjoining diagram, Fig. 37-4, for the first long series.

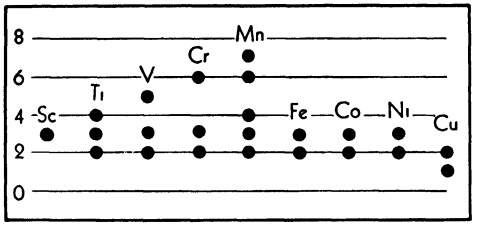


Fig. 37-4. Oxidation States of Several Transition Elements

In general, the transition elements form cations in their lower oxidation states—for example, Mn^{++}, Cr^{+++}, Fe^{+++}, and Fe^{++}—and anions in their higher oxidation states—for example, MnO_4^-, and CrO_4^{--}. Because of the ease with which one of these elements can change from one oxidation state to another, many of their compounds are excellent oxidizing agents or reducing agents.

2. Colored compounds among the transition elements. The absorption spectra of most of the compounds of the transition elements lie in the visible range. As a result, their compounds are colored. Thus the hydrated manganous ion, the cupric ion, the nickelous ion, and the cobaltous ion are pink, blue, green, and rose-colored respectively, while the permanganate ion, MnO_4^-, is deep purple, and the chromate ion, CrO_4^{--}, is yellow. Even among the lanthanides, which are so alike chemically as to make their separation difficult, we find marked differences in color. Thus the salts of praseodymium, Pr, are green, while those of its neighbor, neodymium, Nd, are red.

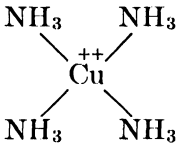
3. Complex ion formation among the transition elements. One of the most striking properties of the transition elements is the ability of their ions to form complex ions. Complex ions are ions composed of more than one atom. Examples are NH_4^+, $Cu(NH_3)_4^{++}$, NO_3^-, and $Cr_2O_7^{--}$. Ions of the transition elements may make use of their inner orbitals to form co-ordinate covalent bonds with other ions or molecules; or they may sometimes form complex ions by attracting polar molecules to them, forming bonds called *ion-dipole* bonds. The complexes found in the $+2$ and $+3$ oxidation states of the transition elements are less stable than the familiar oxygen-complex anions of the higher oxidation states, such as MnO_4^-, and have a tendency to dissociate into simple ions and the complexing molecules:

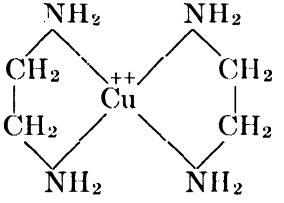
$$Cu(NH_3)_4^{++} \rightleftarrows Cu^{++} + 4\ NH_3$$

Because of the electropositive nature of the $+2$ and $+3$ ions, complex formation takes place with ions or molecules which have unshared pairs of electrons (Lewis bases, p. 347), such as NH_3, H_2O, Cl^-, CN^-, and NO_2^-

Thus the cupric ion, Cu^{++}, combines with 4 ammonia molecules or 4 water molecules to form $Cu(NH_3)_4^{++}$ or $Cu(H_2O)_4^{++}$. A ferrous ion Fe^{++}, will co-ordinate with six cyanide ions, CN^-, to form $Fe(CN)_6^{---}$ while the ferric ion will similarly co-ordinate with six cyanide ions to form $Fe(CN)_6^{---}$, which differs from the former only in the charge on the ion.

Sometimes two or more groups on the same molecule may complex with a single ion; the compound so formed is called a chelate complex. Thus ethylene diamine, $H_2N—CH_2—CH_2—NH_2$, forms a complex ion with copper, analogous to the ammonia complex, as shown below:





Hemoglobin is a chelate complex of iron. A derivative of ethylene diamine known as ethylene diamine tetraacetic acid, is used to form chelate complexes with the ions of hard water.

Co-ordination Number • The co-ordination number of an atom or ion is the number of molecules, atoms, or ions which the atom or ion is able to surround itself with and hold in combination. Thus the co-ordination number of Ag^+ in $Ag(NH_3)_2^+$ is 2, that of copper in $Cu(H_2O)_4^{++}$ is 4, that of Co^{+++} in $Co(NO_2)_6^{---}$ is 6. In the nitrate ion, NO_3^-, the co-ordination number is 3.

There are two factors which appear to determine the co-ordination number of an atom or ion: (1) the size of the atom or ion, and (2) the orbitals available for co-ordination.

As an example of the first of these effects, consider the formulas of the common oxygen acids of nitrogen, phosphorus, arsenic, and antimony in the oxidation state of +5. In the absence of any evidence to the contrary, one might expect the corresponding hydroxides to be $N(OH)_5$, $P(OH)_5$, $As(OH)_5$, and $Sb(OH)_5$. Instead, we find the stable form of nitric acid to be NO_2OH, which is, hypothetically, formed by removal of two molecules of water from $N(OH)_5$. Phosphoric acid, on the other hand, can exist, and normally does exist, as H_3PO_4, or $PO(OH)_3$. This is related to the hypothetical $P(OH)_5$ by loss of one molecule of water from the latter. The explanation for this difference would appear to be that the nitrogen atom is so small that it can accommodate only three oxygen atoms about it, while the larger phosphorus atom can accommodate four (Fig. 37-5, p. 664).

The common acid of arsenic in its oxidation state of +5 is H_3AsO_4, analogous to that of phosphorus. When we come to antimony, however, the size of the antimony atom is such that it can accommodate not only the five oxygen atoms of $Sb(OH)_5$, but even an extra one, since $Sb(OH)_5$ tends to co-ordinate with a sixth hydroxyl group to form the anion $Sb(OH)_6^-$ (Fig. 37-6).

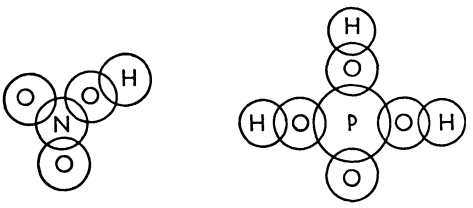


Fig. 37-5. Models of Nitric and Phosphoric Acids Showing Effect of Atom Size on Co-ordination Number

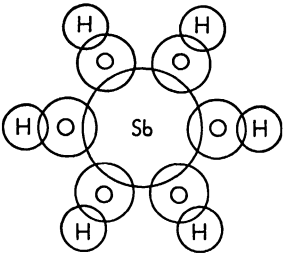


Fig. 37-6. Model of $Sb(OH)_6^-$ Showing Effect of Atom Size on Co-ordination Number

Among the transition elements the co-ordination numbers of the metals in the oxidation states of +2 and +3 are normally larger at the left of a period. Thus the co-ordination numbers of Ti^{+++}, V^{+++}, Cr^{+++}, Fe^{+++} and Fe^{++}, Co^{+++} and Co^{++}, and Ni^{++} are 6, while that of the cupric ion, Cu^{++}, is 4. The silver ion, Ag^+, to the right of the second period has a co-ordination number of only 2. The smaller co-ordination numbers of copper, cadmium, and silver appear to be associated with the number of orbitals available for co-ordination.

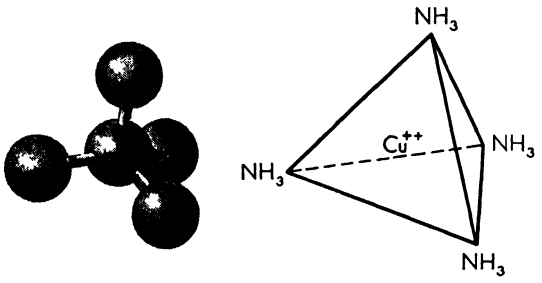


Fig. 37-7. Two Models Showing the Tetrahedral Form of a Co-ordination Complex.

Structure of Co-ordination Complexes · X-ray analysis of crystals of co-ordination complexes shows that those in which the central ion or atom has a co-ordination number of 4 are tetrahedral or planar in form. Thus $Cu(NH_3)_4^{++}$ has the structure shown in Fig. 37-7.

Those complexes in which the central atom or ion has a co-ordination number of six are octahedral; thus the ferrocyanide ion has the structure shown in Fig. 37-8.

The Free Elements—Oxidation State of Zero · Included in the transition elements are many of our most important metals. In the first row of transition elements we find titanium, which has found important use in

the exhaust pipes of jet engines, where its resistance to chemical action at very high temperatures is of great value. Vanadium metal is used in making alloy steels. Chromium steel, because of its resistance to corrosion and its shiny appearance, has found use in plating and in the manufacture of stainless steel. Manganese is used in making alloy steels. Iron, because of its abundance, is by far our most important metal. Cobalt and nickel, and their alloy, monel metal, have many uses, particularly in making alloy steels, while copper is used in coinage, in making wire for the transmission of electricity, and for many other purposes. Transition elements in the second and third rows are not so abundant and, in general, are less reactive. Silver, gold, and platinum are used in coinage and jewelry. Zirconium, tungsten, and molybdenum have their uses in alloys.

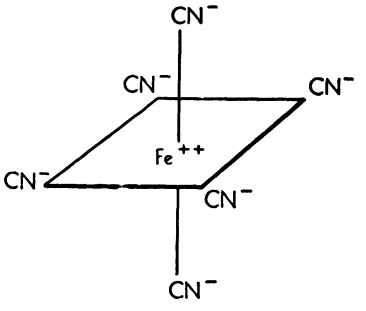


Fig. 37-8

The metallurgy of iron and steel has already been described. Metallurgy of each of the other elements presents its own individual problems. These have been discussed, in a general way, in the chapter on metals and metallurgy. More specific details will be given when the various elements are discussed individually.

Transition Elements: Scandium, Yttrium, and the Rare-Earth Elements

History. In 1794 Gadolin discovered a new mineral, now called *gadolinite*, in the mines of Ytterby, near Stockholm, and found it to contain an oxide unlike any known at that time; this was named *yttria*. This same material has since been found in a great many minerals. Almost at once yttria was recognized as a complex substance, and from that time to the present day many chemists have been engaged in determining its composition. In all, seventeen very similar elements are now clearly recognized to be present in yttria. Two, scandium and yttrium, fall into regular places in the periodic table. The other fifteen have consecutive atomic numbers, 57–71. Their oxides are known collectively as the *rare earths*, and the elements are called the *rare-earth elements* (or *metals*).

These elements caused a good deal of confusion because their properties are such that all belong in the same position in the periodic table. In the light of modern knowledge of atomic structure, this apparently anomalous situation finds a logical explanation (p. 661).

Occurrence. Minerals containing these elements have been found in many different countries, including the United States. Some of these elements, for which delicate spectroscopic tests are known, are found to be widely distributed in many minerals, but in any appreciable quantities they are only of very local occurrence. As far as is known, no one of them ever occurs by itself, and a mineral which contains one is likely to contain most of them.

General characteristics. A number of reactions are known which separate these elements as a group more or less completely from all others, but no one of the rare earths, with the exception of cerium, can be separated from the others by a single precipitation of the usual kind. Separations are effected by fractional recrystallizations or precipitations repeated hundreds and often thousands of times. Two new methods of separation, developed in recent years, show more promise: (1) the oxidation or reduction of some of the elements to other than the trivalent state and (2) the use of ion-exchange reactions similar to those used in water purification (p. 790).

These elements are all trivalent, although a few of them are bivalent as well, and cerium is often tetravalent. In general, they resemble aluminum, but their hydroxides are stronger bases, their salts are less hydrolyzed, and they form no alums. The salts of about half of these elements are colorless; those of neodymium are red, those of praseodymium green, those of samarium yellow, those of europium and terbium rose, and the ceric salts yellow or red.

ELECTRON CONFIGURATIONS OF THE RARE-EARTH ELEMENTS*

ATOMIC NUMBER	ELEMENT	ELECTRONS IN SHELLS	ATOMIC WEIGHT
57	Lanthanum (La)	2, 8, 18, 18, 9, 2	138.92
58	Cerium (Ce)	2, 8, 18, 20, 8, 2	140.13
59	Praseodymium (Pr)	2, 8, 18, 21, 8, 2	140.92
60	Neodymium (Nd)	2, 8, 18, 22, 8, 2	144.27
61	Promethium (Pm)	2, 8, 18, 23, 8, 2	
62	Samarium (Sm)	2, 8, 18, 24, 8, 2	150.43
63	Europium (Eu)	2, 8, 18, 25, 8, 2	152.0
64	Gadolinium (Gd)	2, 8, 18, 25, 9, 2	156.9
65	Terbium (Tb)	2, 8, 18, 27, 8, 2	159.2
66	Dysprosium (Dy)	2, 8, 18, 28, 8, 2	162.46
67	Holmium (Ho)	2, 8, 18, 29, 8, 2	164.94
68	Erbium (Er)	2, 8, 18, 30, 8, 2	167.2
69	Thulium (Tm)	2, 8, 18, 31, 8, 2	169.4
70	Ytterbium (Yb)	2, 8, 18, 32, 8, 2	173.04
71	Lutetium (Lu)	2, 8, 18, 32, 9, 2	174.99

*From W. F. Meggers, *Science* (May 16, 1947), pp. 514–516.

Applications. A few practical applications have been found for some of these substances. By electrolyzing a mixture of a number of their compounds an alloy of the metal is obtained, known as *mixed metal* (*Mischmetall*). The heat of combustion of this alloy is greater than that of aluminum, and it is a more powerful reducing agent. It is therefore sometimes used in place of aluminum in the

Goldschmidt process. An alloy of cerium with iron, known as *Auer metal*, produces brilliant sparks when drawn across a rough surface, and is used in the manufacture of gas-lighters and cigar-lighters. Some salts of cerium are used in medicine. Cerium oxide is a good catalytic agent in many reactions of oxidation, and it is used also in some enamels, and in making special glasses and the luminescent screens in television picture tubes. Other applications are being sought, since at the present time large quantities of the mixed oxides are available.

Transition Elements: The Actinide Series

The element actinium (at. no., 89) falls naturally into Group IIIA of the periodic table; and thorium, protactinium, uranium (at. nos., 90, 91, 92), were formerly placed in Groups IVA, VA, and VIA. When the elements 93, 94, 95, 96, were prepared, by nuclear transformations (p. 357), it was expected that they (as transuranium elements) might occupy Groups VIIA and VIII. But a careful study of the properties of all eight elements led the young American chemist Seaborg to suggest that they are all a part of a new transition series, which is similar to the rare-earth elements (table below). Since then, elements 97 ,98, 99, 100, and 101 have been prepared.

ELECTRON CONFIGURATIONS IN THE ACTINIDE SERIES*

ATOMIC NUMBER	ELEMENT	ELECTRONS IN SHELLS	ATOMIC WEIGHT
89	Actinium (Ac)	2, 8, 18, 32, 18, 9, 2	
90	Thorium (Th)	2, 8, 18, 32, 18, 10, 2	232
91	Protactinium (Pa)	2, 8, 18, 32, 20, 9, 2	231
92	Uranium (U)	2, 8, 18, 32, 21, 9, 2	238.07
93	Neptunium (Np)	2, 8, 18, 32, 22, 9, 2	237
94	Plutonium (Pu)	2, 8, 18, 32, 23, 9, 2	239
95	Americium (Am)	2, 8, 18, 32, 24, 9, 2	243
96	Curium (Cm)	2, 8, 18, 32, 25, 9, 2	243
97	Berkelium (Bk)	2, 8, 18, 32, 26, 9, 2	245
98	Californium (Cf)	2, 8, 18, 32, 27, 9, 2	246
99	Einsteinium (E)	2, 8, 18, 32, 28, 9, 2	255
100	Fermium (Fm)	2, 8, 18, 32, 29, 9, 2	255
101	Mendelevium (Mv)	2, 8, 18, 32, 30, 9, 2	256

*From W. F. Meggers, *Science* (May 16, 1947), pp. 514–516.

All the elements of the actinide series are radioactive; they have no stable isotopes (see the Appendix). For the most part, their main usefulness depends upon their radioactive properties (p. 318).

Elements of the Actinide Series · *Actinium* was discovered by André Debierne in 1899 in *pitchblende*. It precipitates with the rare-earth ele-

ments when they are separated from uranium ores and is difficult to remove from them. The properties of several of its compounds are known. It is the parent substance of a naturally occurring, radioactive disintegration series (pp. 322, 324).

Thorium was discovered by Berzelius in 1828 and named in honor of the Scandinavian god Thor. For the most part, it is found in very small percentages in various minerals, especially those that are rich in the rare earths. Industrially its compounds are obtained from *monazite sand.* This is a heavy sand that consists of cerium phosphate associated with the phosphates of other rare earths and of thorium. The best quality of monazite sand comes from India and Brazil.

Compounds of thorium are obtained from monazite for the manufacture of gas mantles, which consist of 99 per cent of thorium oxide (ThO_2) and 1 per cent of cerium oxide (Ce_2O_3). The production of these mantles has declined greatly in recent years because of the widespread use of electric lights. The chief scientific interest in thorium lies in the fact that the element and all its compounds are radioactive (Chap. 19), like uranium and its compounds. In its chemistry thorium is tetravalent in all its compounds, and always plays the part of a base. The metal itself is very difficult to obtain in really pure form.

Protoactinium is present in all uranium ores. It was discovered in 1917 by Hahn and Meitner and by Soddy and Cranston. A number of its compounds have been described.

Uranium was discovered in 1789 by Klaproth in the ore pitchblende. In that ore it occurs as the oxide U_3O_8. Uranium ores are now found in the United States, Canada, Africa, Czechoslovakia, Russia, the Scandinavian peninsula, and the Far East. The metal is difficult to prepare in pure condition. It is said to resemble nickel in appearance. As an acid-forming element it is similar to chromium, in that it forms salts of the formulas M_2UO_4 and $M_2U_2O_7$, but ordinarily it plays the part of a base-forming element. In this capacity it forms a great variety of salts, the best known of which are a series in which the radical UO_2, known as *uranyl*, acts as a bivalent metal. Examples of these salts are uranyl nitrate, $UO_2(NO_3)_2 \cdot 6\ H_2O$, and uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2\ H_2O$. The oxides of uranium have long been used in making greenish-yellow fluorescent glass and in glazes. The greatest use for uranium seems to be in the production of atomic energy (Chapters 21, 47).

Neptunium, plutonium, and other actinides have been referred to in Chapter 21.

Transition Elements: Titanium, Zirconium, and Hafnium

Titanium · Titanium is very abundant in nature (p. 31) but is nowhere concentrated in large deposits. Its chief ores are *rutile* (TiO_2) and *ilmenite* ($FeTiO_3$). Our supply of these ores comes from Arkansas, Florida, New York, and Virginia. It is found also as a variable constituent of certain iron ores, called *titanic iron ores*, and in small percentages in most igneous rocks. The element is very difficult to prepare in pure condition, melts at about 1800°, and has a specific gravity of 4.5. It has the silvery appearance of a metal and it alloys readily with many metals. An alloy with iron called *ferrotitanium* is made by carbon reduction of a mixture of the oxides of iron and titanium, and is used in making titanium steel.

Titanium dioxide (TiO_2), like silicon dioxide, is an acid anhydride, and forms many titanates resembling the silicates. Ilmenite ($FeTiO_3$) is a metatitanate. Fluotitanic acid (H_2TiF_6) and its salts are well known. The chloride, $TiCl_4$, like silicon chloride, is a colorless fuming liquid which boils at 136.4°.

In the trivalent state titanium acts as a metal and forms salts of which the sulfate, $Ti_2(SO_4)_3$, and the chloride, $TiCl_3$, are examples. These salts are either green or violet in color and are strong reducing agents. The brass-yellow nitride, TiN, is formed at high temperatures by the action of nitrogen on titanium.

The very white, opaque dioxide is the only important industrial compound of titanium. By itself, or more often mixed with other white inert substances, it is a valued component of many white paints.

Zirconium · Zirconium is a rather rare element; it occurs in nature as the oxide, ZrO_2 (*baddeleyite*), or as the well-crystallized orthosilicate, $ZrSiO_4$ (*zircon*). The crystals are sometimes clear and colorless; sometimes they are tinted blue, yellow, or red and are classed as semiprecious gems. Australia, India, and Brazil supply nearly all the world's zircon, while in Brazil there is a large deposit of the oxide. The free element is difficult to obtain. An alloy of iron and zirconium (*ferrozirconium*) is used in the steel industry.

Zirconium is tetravalent in nearly all its compounds and forms acids similar to those of titanium; but its metallic properties recall those of tin, for it forms salts in which it acts as a tetravalent metal. Most of these salts are derived from the partial anhydride $ZrO(OH)_2$ and are therefore basic salts. Zirconyl chloride ($ZrOCl_2$) is an example of such a

salt. Zirconium oxide is one of the most infusible oxides. It melts at about 2700°. It is used in making crucibles and tubes for high-temperature use, and bricks (zircite) for lining furnaces. Like tin oxide, it has been used for making enamels, glazes, and opaque white glass.

Hafnium · Hafnium was discovered in 1923 by Coster and Von Hevesy. It is usually found with zirconium, to which it bears a close resemblance.

Other Transition Elements

The chemistry of other transition elements will be discussed in Chapters 38–41.

QUESTIONS

1. (*a*) What are the transition elements? (*b*) What common properties do they have? (*c*) How do you account for the fact that they all show these properties?

2. (*a*) What are the rare-earth elements? (*b*) Account for their remarkable similarities.

3. Account for the atomic structures of the transition elements in terms of subshells and orbitals.

4. What is (*a*) a complex ion? (*b*) a co-ordination compound? (*c*) Distinguish between a complex ion of the sulfate or nitrate type and one of the ferrocyanide type.

5. Define the terms (*a*) *co-ordination number*; (*b*) an *orbital.*

CHAPTER 38

THE IRON FAMILY

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Iron (Fe)	55.85	26	7.86	1535°	2, 8, 14, 2
Cobalt (Co)	58.94	27	8.9	1480°	2, 8, 15, 2
Nickel (Ni)	58.69	28	8.90	1452°	2, 8, 16, 2

The Family · The relationship between iron, cobalt, and nickel is different from that existing among the members of any family so far considered. Their atomic weights are very close together, and in the periodic table they are placed in one family because they are very similar and evidently constitute a natural group. An examination of the electronic structures of the atoms of these elements, as determined by an analysis of their spectra, shows that while they have atomic numbers of 26, 27, and 28 respectively, and consequently 26, 27, and 28 electrons, the outermost shells have two electrons in each case, with the extra electrons of the cobalt and nickel in the incomplete next lower shell. As a result, the physical and chemical properties of these elements are very similar. They are *transition elements* in the first long period (p. 333) and can be expected (1) to have variable valence, (2) to form stable complex ions, and (3) to form colored compounds. This is the case. All three elements show positive valences of 2 and 3, form many complex ions, and their salts are colored.

TRANSITION ELEMENTS
(Elements in which inner shells are being filled to 18 or 32 electrons)

45.10 **Sc** 21	47.90 **Ti** 22	50.95 **V** 23	52.01 **Cr** 24	54.93 **Mn** 25	55.85 **Fe** 26	58.94 **Co** 27	58.69 **Ni** 28	63.54 **Cu** 29
88.92 **Y** 39	91.22 **Zr** 40	92.91 **Nb** 41	95.95 **Mo** 42	**Tc** 43	101.7 **Ru** 44	102.91 **Rh** 45	106.7 **Pd** 46	107.880 **Ag** 47
Rare-Earth Elements 57-71	178.6 **Hf** 72	180.88 **Ta** 73	183.92 **W** 74	186.31 **Re** 75	190.2 **Os** 76	193.1 **Ir** 77	195.23 **Pt** 78	197.2 **Au** 79
Actinide Series 89-96								

Transition Elements in Which an Electron Shell of 8 Is Being Filled to 18 or 32

Compounds of Iron

Two Oxidation Series · Iron differs from the metals studied (Chaps. 17 and 36) in that it forms *two series* of compounds. In one series the iron

is *bivalent* and forms compounds which, in formulas and many chemical properties, are similar to the corresponding zinc compounds. These are called *ferrous* compounds. In the other series iron acts as a *trivalent* metal and forms salts similar to those of aluminum. These salts are known as *ferric* compounds. The compounds of iron in these two valence states are of about equal stability and can be converted from one oxidation state to the other with mild oxidizing and reducing agents. Iron of both valences is present also in many complex salts.

Ferrous Compounds · The ferrous salts resemble those of zinc. They are not greatly hydrolyzed in solution, for ferrous hydroxide is about as strong a base as the hydroxide of zinc; but they are readily oxidized, as will be explained later. The soluble salts (usually green in color) are easily prepared by dissolving iron in the appropriate acid, and the insoluble salts by precipitation.

Ferrous Oxide (FeO); Ferrous Hydroxide (Fe(OH)$_2$) · Ferrous oxide may be obtained as a black combustible powder, by heating ferrous oxalate:

$$FeC_2O_4 \longrightarrow FeO + CO_2\uparrow + CO\uparrow$$

When a solution of a ferrous salt is treated with a soluble base, a white precipitate forms, which is a colloidal gel of the hydroxide, $Fe(OH)_2$. If this is exposed to air and moisture, it quickly oxidizes to a hydrated ferric oxide.

Ferrous Chloride (FeCl$_2$) · Anhydrous ferrous chloride is prepared by strongly heating iron in a current of hydrogen chloride. The salt condenses in the colder portions of the tube in white pearly scales. It dissolves in water, with the evolution of much heat, and from this solution there crystallizes the green tetrahydrate, $FeCl_2 \cdot 4\ H_2O$. The latter salt is more easily obtained by dissolving iron in hydrochloric acid and crystallizing the solution out of contact with the air.

Ferrous Sulfate (FeSO$_4$) · The sulfate is the most familiar ferrous salt and has many uses. It is easily prepared by dissolving iron in dilute sulfuric acid and evaporating until crystallization occurs. It is then obtained in large monoclinic crystals of the composition $FeSO_4 \cdot 7\ H_2O$, known as *green vitriol* or *copperas*. In the industries it is obtained from the liquors which result from cleaning sheet steel with sulfuric acid preparatory to tinning or galvanizing the steel. It is manufactured also by the oxidation of the abundant mineral pyrite (FeS_2), usually after a careful partial roasting, which converts the pyrite into ferrous sulfide (FeS):

$$FeS + 2\ O_2 \longrightarrow FeSO_4$$

It is used as a disinfectant, as a reagent for killing weeds, in the dyeing industry, as a substitute for aluminum sulfate in water purification, and in the manufacture of black inks.

The Vitriols · The term *vitriol* is applied to the hydrated sulfates of a number of bivalent metals. These compounds are of two distinct types: the one group forms monoclinic crystals which contain 7 molecules of water of hydration; the other forms triclinic crystals with 5 molecules of water. All the salts in a given series are isomorphous, and many of the vitriols are dimorphous, crystallizing in both forms. The sulfates of iron, zinc, and magnesium are the most familiar representatives of the monoclinic vitriols, while copper sulfate ($CuSO_4 \cdot 5\,H_2O$) is the best-known triclinic vitriol.

Ferrous Sulfide (FeS) · Ferrous sulfide is found in nature as the yellowish-brown mineral *pyrrhotite*, which nearly always contains an excess of sulfur in solid solution, amounting sometimes to as much as 6.5 per cent of the weight of the mineral. It is easily prepared by heating iron with sulfur or by treating a solution of a ferrous salt with a soluble sulfide:

$$FeCl_2 + (NH_4)_2S \longrightarrow FeS\downarrow + 2\,NH_4Cl$$

Prepared in the latter way, it is a black precipitate, insoluble in water but readily soluble even in very weak acids. It melts at about 1190° and is obtained as a liquid flux in some metallurgical processes. It is used in the laboratory in the preparation of hydrogen sulfide.

Iron Disulfide (FeS$_2$) · This compound occurs very abundantly in nature, especially in Spain. It is found also in the coal measures, often forming fossils of plants. The usual form is called *pyrite*, *pyrites*, or *fool's gold*, and is a brass-yellow mineral, well crystallized in the isometric system. Pyrite is mined in very large quantities and is used as a source of sulfur dioxide in the sulfuric acid industry.

Ferrous Carbonate (FeCO$_3$) · As *siderite*, isomorphous with calcite, ferrous carbonate occurs rather abundantly in nature, often in large crystals. Prepared by precipitation, it is a nearly white crystalline powder. Like calcite, it dissolves in water containing carbon dioxide, with the formation of an acid salt; and solutions of this kind constitute the *chalybeate mineral waters*.

Ferrous Ammonium Sulfate ($(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6\,H_2O$) · When ammonium sulfate and ferrous sulfate are brought together in solution in molecular proportions, a double salt of the formula $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6\,H_2O$, known as *Mohr's salt*, separates on crystallization. This salt oxidizes less readily in the air than most other ferrous salts and is frequently employed in chemical analysis. All the sulfates which form vitriols yield similar double salts, not only with ammonium sulfate, but also with the sulfates of potassium, rubidium, and cesium.

There are therefore many double salts represented by the general formula $\overset{+1}{M}_2SO_4 \cdot \overset{+2}{M}SO_4 \cdot 6\ H_2O$, all of which are isomorphous. (The superscripts (+ 1, + 2) indicate the oxidation state.)

Ferric Compounds · In the ferric compounds iron acts as a trivalent metal; consequently the formulas of these compounds resemble those of the corresponding compounds of aluminum. All the simple ferric salts are largely hydrolyzed, their solutions acquiring the reddish-brown color of the hydroxide.

Ferric Hydroxide ($Fe(OH)_3$) · The only definitely proved crystalline hydroxide of iron known has the composition $FeO \cdot OH$ (or $Fe_2O_3 \cdot H_2O$). When a solution of a base is added to a solution of a ferric salt, a reddish-brown precipitate is formed, which for convenience is given the formula $Fe(OH)_3$. Like the corresponding compound of aluminum (p. 742), it is a colloidal gel, and its composition varies with the exact conditions of its preparation. It may be regarded as an oxide with a varying degree of hydration. Iron rust is probably a mixture of such hydrated oxides.

Ferric Oxide (Fe_2O_3) · When the hydroxide is strongly heated, it forms the oxide Fe_2O_3, which is an insoluble red material occurring in nature in various forms of hematite, which range in color from red to black. The same compound is obtained by burning pyrite and, when carefully prepared, constitutes the pigment called *Venetian red.* Owing to its permanency, this is much used for painting structures that are exposed to the weather, such as bridges and railway cars. Ferric oxide is also found in nature, in combination with ferrous oxide, as the mineral *magnetite,* or *lodestone* (Fe_3O_4). This formula may be written $FeO \cdot Fe_2O_3$.

Ferric Chloride ($FeCl_3$) · Ferric chloride is obtained in anhydrous form as a sublimate by heating iron in a current of chlorine. It is readily formed in solution by the usual methods, and crystallizes in a number of hydrated forms, of which the usual one has the formula $FeCl_3 \cdot 6\ H_2O$. It is very soluble in water and to a less extent in other solvents, such as alcohol and ether. Its solution in dilute alcohol constitutes the ordinary *tincture of iron* of the druggist.

Other Soluble Ferric Salts · Of the other soluble ferric salts a few deserve special mention. The *sulfate,* $Fe_2(SO_4)_3$, can be obtained by the oxidation of green vitriol, as a white poorly crystallized substance. With the alkaline sulfates it forms a series of violet-colored alums, which, owing to their well-crystallized condition, are the ferric salts most frequently used. The most familiar one is the *ferric ammonium alum,* $NH_4Fe(SO_4)_2 \cdot 12\ H_2O$. The *nitrate* is deposited from concentrated solutions in well-formed, deliquescent crystals of the formula $Fe(NO_3)_3 \cdot 6\ H_2O$, which have the same violet color as the alums.

It is moderately soluble in dilute nitric acid, but readily forms supersaturated solutions. Potassium thiocyanate (KCNS) forms a complex thiocyanate when added to a ferric salt, which gives a blood-red color to the solution.

Oxidation of Ferrous Compounds · When exposed to the action of oxidizing agents, especially in the presence of water, ferrous compounds are readily oxidized to the corresponding ferric compounds:

$$4\ FeO + O_2 \longrightarrow 2\ Fe_2O_3$$
$$4\ Fe(OH)_2 + 2\ H_2O + O_2 \longrightarrow 4\ Fe(OH)_3$$
$$4\ FeSO_4 + 2\ H_2SO_4 + O_2 \longrightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2O$$

In moist air the oxidation produces a basic ferric sulfate, thus:

$$4\ FeSO_4 + 2\ H_2O + O_2 \longrightarrow 4\ FeSO_4(OH)$$

Oxidation and Reduction of Iron Salts · The oxidation of iron from the *ferrous* (Fe^{++}) condition to its higher state of oxidation (*ferric*, Fe^{+++}), by an oxidizing agent such as chlorine, as shown in the equation

$$2\ FeCl_2 + Cl_2 \longrightarrow 2\ FeCl_3$$

may also be represented in terms of ions and the charges which they carry,

$$2(Fe^{++},\ 2\ Cl^-) + Cl_2 \longrightarrow 2(Fe^{+++},\ 3\ Cl^-)$$

or in terms of electronic partial equations:

Oxidation	$2 \times (Fe^{++} \longrightarrow Fe^{+++} + e^-)$
Reduction	$Cl_2 + 2\ e^- \longrightarrow 2\ Cl^-$
Essential ionic reaction	$2\ Fe^{++} + Cl_2 \longrightarrow 2\ Fe^{+++} + 2\ Cl^-$

In reactions of this type the substance reduced (chlorine) is called the *oxidizing agent*, and the substance oxidized (ferrous ion) the *reducing agent* (p. 209).

In like manner, the equation for the reduction of ferric iron by metallic iron may be written in ionic form to show the loss and gain of electrons:

$$2\ FeCl_3 + Fe \longrightarrow 3\ FeCl_2$$
$$2(Fe^{+++},\ 3\ Cl^-) + Fe \longrightarrow 3(Fe^{++},\ 2\ Cl^-)$$

Oxidation	$Fe \longrightarrow Fe^{++} + 2\ e^-$
Reduction	$2 \times (Fe^{+++} + e^- \longrightarrow Fe^{++})$
Essential ionic reaction	$Fe + 2\ Fe^{+++} \longrightarrow 3\ Fe^{++}$

Complex Compounds of Iron · Iron forms a large number of complex compounds, of which the cyanides only will be described. Iron forms no simple cyanides, but a very large number of complex cyanides are known, of which the ferrocyanide and ferricyanide of sodium and of potassium are the most important.

Sodium Ferrocyanide, $Na_4Fe(CN)_6$; Potassium Ferrocyanide, $K_4Fe(CN)_6$ · These two compounds are salts of the unstable ferrocyanic acid, $H_4Fe(CN)_6$. They are prepared from by-products obtained in the manufacture of coke.

When coal is heated in the absence of air, small amounts of the carbon, nitrogen, and hydrogen present are evolved in the form of hydrogen cyanide. This is absorbed and converted into calcium ferrocyanide by means of calcium hydroxide and the spent iron oxide employed in the purification of the gas evolved in the coking of the coal. The calcium ferrocyanide so obtained is converted into sodium or potassium ferrocyanide by treatment with appropriate salts of sodium or potassium. The reactions involved in the complete process are complex.

Both sodium ferrocyanide and potassium ferrocyanide are yellow in color and are readily soluble in water. The latter compound is often called *yellow prussiate of potash*. The sodium salt crystallizes from water in the form of the hydrate $Na_4Fe(CN)_6 \cdot 10\ H_2O$, while the potassium salt crystallizes as the hydrate $K_4Fe(CN)_6 \cdot 3\ H_2O$. In solution they ionize as follows:

$$Na_4Fe(CN)_6 \longrightarrow 4\ Na^+ + Fe(CN)_6^{----}$$
$$K_4Fe(CN)_6 \longrightarrow 4\ K^+ + Fe(CN)_6^{----}$$

It is important to notice that the ions of iron are not present in sufficient concentration to give the ordinary reactions for iron.

Potassium Ferricyanide, $K_3Fe(CN)_6$ · When potassium ferrocyanide in solution is treated with an oxidizing agent, a solution is obtained, from which crystallize garnet-red crystals of the composition $K_3Fe(CN)_6$, known as *potassium ferricyanide* or *red prussiate of potash*. With chlorine as the oxidizing agent the equation is as follows:

$$2\ K_4Fe(CN)_6 + Cl_2 \longrightarrow 2\ K_3Fe(CN)_6 + 2\ KCl$$

This compound in solution gives the ions $3\ K^+$ and $Fe(CN)_6^{---}$ but an inappreciable concentration of iron ions. Potassium ferricyanide is a salt of the unstable ferricyanic acid, $H_3Fe(CN)_6$.

Other Complex Cyanides · Since the potassium in both ferrocyanide and ferricyanide acts as an ion, it is replaceable by other metals through double decomposition. Most of the ferrocyanides and ferricyanides so obtained are colloidal compounds insoluble in water and dilute acids. Copper ferrocyanide may be precipitated in a porous porcelain wall and used as an osmotic membrane (p. 203). The compounds obtained by treating potassium ferrocyanide and potassium ferricyanide with simple ferrous and ferric salts are of special interest.

With potassium ferrocyanide and ferric chloride the equation is

$$3\ K_4Fe(CN)_6 + 4\ FeCl_3 \longrightarrow Fe_4(Fe(CN)_6)_3\downarrow + 12\ KCl$$

The complex product of this reaction is an indigo-blue precipitate, known as *ferric ferrocyanide* or *Prussian blue.* It is used largely as a pigment.

With potassium ferricyanide and ferrous sulfate the equation is

$$2\ K_3Fe(CN)_6 + 3\ FeSO_4 \longrightarrow Fe_3(Fe(CN)_6)_2\downarrow + 3\ K_2SO_4$$

The resulting complex is of much the same color as Prussian blue and is known as *ferrous ferricyanide* or *Turnbull's blue.* The formation of these two precipitates affords a delicate method not only for detecting the presence of iron in the form of its salts but also for distinguishing between ferrous and ferric salts.

Blueprinting · When a ferric salt and potassium ferricyanide are brought together in solution, no precipitate forms, though the solution acquires a brownish color. On exposure to the sunlight, the ferric salt undergoes a partial reduction to ferrous salt, and a blue precipitate forms. Advantage is taken of these facts in the process of blueprinting. A sensitive surface is prepared by soaking paper in a solution of potassium ferricyanide and a ferric salt (ferric ammonium citrate is generally used), and drying it in a dark place. When a black drawing on tracing cloth is placed upon such a sensitized paper and the two are exposed to the sunlight, the sensitized paper (except where it is protected by the black lines) turns a brownish color. It is then thoroughly washed with water to remove the soluble salts, the portions acted upon by the light turning blue, while the unaffected portions are left white. Both Prussian blue and Turnbull's blue are decomposed and thus decolorized by soluble bases, so that a solution of sodium hydroxide can be used as an ink for white lettering on a blueprint.

Ferric salts give a black precipitate with solutions of gallic acid (present in *nutgalls*), as well as with solutions of tannin (present in tea and in the barks of various trees). Advantage is taken of this reaction in the preparation of certain grades of black inks.

Cobalt

Occurrence · Most minerals containing cobalt are strongly suggestive of the presence of a heavy metal; yet the older metallurgists were unable to smelt them and obtain this metal. For this reason they named the metal *kobold,* meaning "goblin," and this gave us our name *cobalt.* The metal was finally obtained by the Swedish chemist Brandt in 1735. Cobalt usually occurs in combination with arsenic and sulfur, in complex minerals which also contain silver, iron, nickel, and copper. The simplest of these is *cobaltite* (CoAsS). Such minerals are found sparingly in many localities, but the richest known deposits are those located at Cobalt, Ontario, and in Africa. These are very rich in silver, and cobalt is worked up as a by-product, together with nickel and arsenic trioxide. In the Belgian Congo, cobalt is a by-product of copper-refining.

Metallurgy and Properties · The metallurgy of the metal is very complicated, since it is difficult to separate cobalt and nickel. The pure metal is best prepared by the Goldschmidt process. It is a malleable, magnetic, silvery metal, which soon takes on a reddish tint upon exposure to the air. The metal is used chiefly in the form of alloys. *Cobalt chromium steels*, collectively known as Stellite, are used extensively in making high-speed cutting tools, since they retain their temper at high temperatures, and as important rust-resisting alloys. They are often modified by additions of tungsten, molybdenum, and nickel. An alloy called Konel contains cobalt, nickel, and ferrotitanium, and is harder than steel even when very hot. Metallic cobalt is used as a binding material for crystals of tungsten carbide in making the hard cutting material Carboloy (p. 699).

Oxides of Cobalt · Cobaltous oxide, CoO, is the chief oxide of cobalt. In addition to this it forms two other oxides, Co_2O_3 and Co_3O_4, corresponding to those of iron. Cobaltous oxide is a black powder used in making other cobalt compounds, blue glass, and blue decorations on china. When used as an ingredient in glasses, glazes, and enamels, it forms a blue silicate which has intense coloring properties. Sometimes the powdered blue glass called *smalt* is used instead of the oxide, and also as a pigment. In very small quantities it is used to correct the natural yellow color of clay, just as bluing whitens linen.

Salts of Cobalt · Cobalt forms two series of compounds, as does iron, in the oxidation states $+2$ and $+3$. However, in the bivalent state the compounds of only the *simple* salts of cobalt are stable, while in the trivalent state only the *complex* compounds are stable. Cobaltous compounds in anhydrous form are blue, but when hydrated they are usually cherry-red. The hydrated *cobaltous nitrate*, $Co(NO_3)_2 \cdot 6\ H_2O$, and *cobaltous chloride*, $CoCl_2 \cdot 6\ H_2O$, are the salts most frequently employed in the laboratory; both these salts are cherry-red in color. The *sulfide*, CoS, is formed as a black precipitate when a cobalt salt is treated with ammonium sulfide. It dissolves slowly in dilute acids, but much more rapidly in concentrated ones. The *simple* salts derived from cobaltic oxide, corresponding to the ferric salts, are very unstable, and few are well known. There are, however, a great many complex cobaltic salts. Some organic salts of cobalt are used as driers in paints.

Complex Compounds of Cobalt · Cobalt, especially in the trivalent state, forms a variety of complex ions by adding six ions or molecules to one cobaltic ion. The most common of these are the cobaltammine ions. All these are highly colored ions which may be considered to be formed from the ion $Co(NH_3)_6^{+++}$ by the substitution of one or more ammonia molecules by another ion or molecule.

If the other substance is, for example, the nitrite ion (NO_2^-), then ions may be prepared having the formulas

$Co(NH_3)_5(NO_2)^{++}$ nitropentammine cobalt (III) ion
$Co(NH_3)_4(NO_2)_2^+$ dinitrotetrammine cobalt (III) ion
$Co(NH_3)_3(NO_2)_3$ trinitrotriammine cobalt (III)
$Co(NH_3)_2(NO_2)_4^-$ tetranitrodiammine cobaltate (III) ion
$Co(NO_2)_6^{---}$ hexanitrocobaltate (III) ion, or cobaltinitrite ion

Note that the charge on the complex ion is the sum of the three positive charges on the cobalt ion and the single negative charge on the nitrite ion, and the electrovalence of the complex ion changes from + 3 in $Co(NH_3)_6^{+++}$ through 0 to − 3 in $Co(NO_2)_6^{---}$, although the ion of charge − 2 is not known. Many other ions or molecules may be present in place of the nitrite ion in the positive complex ions—for example, ions of the formulas $Co(NH_3)_5(H_2O)^{+++}$ $Co(NH_3)_5(OH)^{++}$, $Co(NH_3)_4Cl_2^+$, and $Co(NH_3)_4(CO_3)^+$.

The last ion of the series above, $Co(NO_2)_6^{---}$, forms an insoluble yellow salt, $K_3Co(NO_2)_6$, with potassium ions, and is used as a test for the presence of potassium. It is easily formed by the oxidation of the cobaltous ion by the nitrite ion in the presence of hydrogen and potassium ions:

$$3\ K^+ + Co^{++} + 7\ NO_2^- + 2\ H^+ \longrightarrow K_3Co(NO_2)_6 + NO + H_2O$$

Nickel does not form a precipitate with these reagents, and the reaction may be used to separate cobalt and nickel from each other.

Nickel

Occurrence and Production · The early metallurgists were acquainted with certain minerals of high metallic luster, strongly resembling the ores of copper, but from which they could not extract that metal, and which they accordingly named *kupfernickel*, or false copper. The labors of Cronstedt and Bergman in Sweden, toward the close of the eighteenth century, resulted in the isolation of the new metal and its clear differentiation from cobalt.

Nickel is almost always associated with cobalt in nature. Like the latter element, it occurs in combination with sulfur and arsenic and is often associated with copper, silver, and iron. Most of its ores are very complex. It was formerly obtained, chiefly as a by-product, in the metallurgy of copper and silver. At present most of the world's supply comes from the Sudbury district in Ontario, Canada. There the nickel occurs in the mineral pyrrhotite (a sulfide of iron, p. 673) and is associated with chalcopyrite, the nickel-copper content being from 10 to 20 per cent. The Sudbury minerals contain small percentages of platinum, palladium, and iridium, and are a large source of these rare metals. The extraction of nickel from its ores is a complicated process.

Properties and Uses · Nickel is a silvery metal capable of taking a very high polish. It is very hard, but is quite malleable. It can be welded on iron, and the two rolled into sheets for making various kitchen utensils. Like iron and cobalt, it is magnetic. It is not attacked by melted alkalies; hence nickel crucibles are often employed in the laboratory for alkali fusions. The nonoxidizing acids evolve hydrogen with nickel very slowly, but nitric acid dissolves it readily.

In many countries, pure nickel is used for subsidiary coinage for a total of several billion coins. In the form of a fine powder it is a most effective catalyst in reactions in which hydrogen is added to an organic compound, as in the hydrogenation of oils (p. 538). It has been used extensively for electroplating on other metals, such as iron, brass, or copper, to prevent tarnishing. Chromium plating is largely replacing it, but a preliminary plating with nickel usually precedes plating with chromium. For nearly all other purposes it is used as an alloy metal.

Alloys of Nickel · The older alloys were (1) for coinage, the United States using a five-cent piece containing 25 per cent nickel, and 75 per cent copper and (2) for German silver, containing 20 per cent nickel, 55 per cent copper, and 25 per cent zinc. For about fifteen years before the war of 1914–1918 nearly all the nickel produced went into armor plate, gun castings, and all sorts of ordnance equipment. Since that time many new uses for nickel as an alloy metal have been developed. The nickel alloys, a great many of which have special trade names, may be classified as follows:

1. Low-nickel steel and cast iron, from $1\frac{1}{2}$ to 5 per cent nickel, for structural purposes, castings, and machinery parts.

2. Ferronickel alloys, from 35 to 80 per cent nickel, for electrical and magnetic uses.

3. Nickel-chromium-iron structural steel, from $1\frac{1}{2}$ to 5 per cent nickel, for automobiles and heavy machinery.

4. Noncorrosive (stainless) steel, containing chromium together with from 7 to 35 per cent nickel.

5. Nonferrous alloys, of which some four hundred are listed, the best-known being *monel metal*. This alloy consists approximately of 70 per cent nickel, 28 per cent copper, and 2 per cent iron. It is produced directly from the copper-nickel ores without separating the metals, and varies somewhat in composition. It is a silvery, malleable metal much used for sinks, dairy equipment, and soda fountains, and for many purposes where cleanliness and resistance to mild corrosion are imperative.

Compounds of Nickel · Nickel forms four oxides, of the formulas NiO, Ni_2O_3, NiO_2, and Ni_3O_4. Nickel forms only one series of compounds with elements other than oxygen; in these it is bivalent, corresponding to the ferrous salts. When anhydrous, these compounds are usually yellow; when hydrated, some shade of deep green.

Salts of Nickel · *Nickel sulfide* (NiS), as prepared by precipitation, is a black amorphous powder, insoluble in water and dilute acids but easily soluble in more concentrated acids. *Nickel chloride* ($NiCl_2 \cdot 6\ H_2O$), *nickel nitrate* ($Ni(NO_3)_2 \cdot 6\ H_2O$), and *nickel sulfate* ($NiSO_4 \cdot 7\ H_2O$) are the most familiar simple salts of this metal. The sulfate also forms crystals of the composition $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6\ H_2O$, corresponding to Mohr's salt. It is the salt of nickel employed as the electrolyte in nickel-plating, a piece of pure nickel being used as the anode and the object to be plated as the cathode. There are many complex salts of nickel.

Nickel Carbonyl, Ni(CO)$_4$ · When carbon monoxide is passed over metallic nickel at a temperature between 30° and 50°, the two unite to form a compound of the formula $Ni(CO)_4$, known as nickel carbonyl. It is a colorless liquid, boiling at 43.2°, and freezing at −25° to colorless, needle-shaped crystals. When the vapor of the compound is passed through a tube heated to above 100°, the compound dissociates into the metal and carbon monoxide. Advantage is taken of this reaction in the Mond process for purifying nickel.

Carbonyls of the Other Metals · Cobalt forms two carbonyls, $Co_2(CO)_8$ and $Co_4(CO)_{12}$, but both of these are solids and are formed only under pressure. Iron forms three, $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$. Of these the pentacarbonyl is a yellow liquid, freezing at −21° and boiling at 103°. When heated, iron carbonyls decompose like the nickel compound, and very pure iron can be obtained in this way.

QUESTIONS

1. Define and give examples, where possible, of each of the following: (*a*) ferrous salt; (*b*) ferric salt; (*c*) a vitriol; (*d*) a double salt; (*e*) a complex salt; (*f*) a complex ion.

2. Describe the process of blueprinting, explaining the principles involved. What is the formula of the blue compound formed in the process?

3. What sort of a reagent is needed in order to change a ferrous ion to a ferric ion? a ferric ion to a ferrous ion? Name several reagents which might bring about each of these changes.

4. Complete and balance each of the following equations:

a. $Fe^{++} + H^+ + NO_3^- \longrightarrow$

b. $Fe^{++} + H^+ + MnO_4^- \longrightarrow Mn^{++} +$

c. $Fe^{+++} + H_2S + \longrightarrow Fe^{++} + S +$

d. $Fe^{++} + K_3Fe(CN)_6 \longrightarrow$

e. $Fe^{+++} + K_4Fe(CN)_6 \longrightarrow$

f. $K^+ + Co^{++} + NO_2^- \longrightarrow K_3Co(NO_2)_6 + NO$

5. How might one prepare ferrous chloride without the use of hydrochloric acid or metallic iron?

6. In the electrolysis of ferric nitrate the salt is reduced to ferrous nitrate at the cathode. Write the ionic equation.

7. (*a*) Why should the properties of iron, cobalt, and nickel be similar?

(*b*) Does each of the elements form stable series of salts in the bivalent and trivalent state?

8. Given iron pyrite, air, coke, and water, show by equations how you could prepare ferrous sulfate.

9. What analytical test can be used to distinguish between (*a*) Fe^{++} and Fe^{+++} ions; (*b*) Fe^{+++} and Co^{++} ions; (*c*) Co^{++} and Ni^{++} ions; (*d*) Fe^{++} and Ni^{++} ions?

10. What are the transition elements? What properties do they have?

11. Pyrite is an abundant mineral, mined in large quantities. Why is it not used as a source of iron?

PROBLEMS

1. What volume of sulfuric acid of density 1.84 and containing 98 per cent of hydrogen sulfate will be required (in addition to an oxidizing agent) to convert 1 kg of ferrous sulfate into ferric sulfate?

2. What weight of hydrogen chloride can be obtained by the reduction of 1 kg of ferric chloride to ferrous chloride by nascent hydrogen?

3. Nine hundred grams of ferric chloride in solution was converted into ferrous chloride by the reducing action of iron. How much ferrous chloride was obtained?

4. Which contains the greater percentage of iron: $Na_4Fe(CN)_6 \cdot 10\ H_2O$ or $K_4Fe(CN)_6 \cdot 3\ H_2O$?

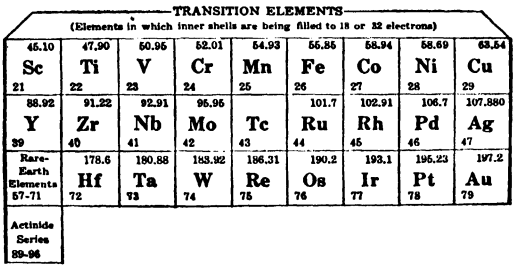
5. Nitric acid oxidizes iron to ferric nitrate. What volume of nitric acid of density 1.4 will be required to prepare 1 kg. of crystallized ferric nitrate? (Assume that nitric acid acts on iron as on zinc.)

CHAPTER 39

SOME METALLO–ACID ELEMENTS

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Vanadium (V) . . .	50.95	23	5.96	1710°	2, 8, 11, 2
Chromium (Cr) . . .	52.01	24	7.1	1615°	2, 8, 12, 2
Manganese (Mn) . .	54.93	25	7.2	1260°	2, 8, 13, 2
Niobium (Nb) . .	92.91	41	8.4	1950°	2, 8, 18, 11, 2
Molybdenum (Mo) .	95.95	42	10.2	2625°	2, 8, 18, 12, 2
Technetium (Tc) . .	97 (?)	43	—	—	2, 8, 18, 13, 2
Tantalum (Ta) . . .	180.88	73	16.6	2996°	2, 8, 18, 32, 11, 2
Tungsten (W) . . .	183.92	74	19.3	3370°	2, 8, 18, 32, 12, 2
Rhenium (Re) . . .	186.31	75	—	3440°	2, 8, 18, 32, 13, 2

The Elements · The elements in the table above are transition elements. As transition elements, they have the characteristics common to that group; namely, they (1) have a marked tendency to exist in several oxidation states, (2) form very stable complex ions, and (3) form brightly colored compounds. These elements are typical metals in their physical properties, while in their chemical characteristics they can all act as acid-forming elements. Hence they are sometimes called metallo-acid elements.



Transition Elements

At least three of these elements, chromium, manganese, and rhenium (and possibly technetium), form many salts in which the metal atoms are simple cations, as well as salts in which the atoms of the elements are in the anions. In the other five elements in the table (we exclude technetium) the tendency to form simple cations of salts is either absent altogether or rather feebly developed.

It is convenient to study chromium and manganese (and rhenium and technetium) together as one group and the other five elements as a second group.

Chromium and Manganese

General · Chromium and manganese have many characteristics in common. Both have more than two oxidation states: chromium, $+2$, $+3$, and $+6$; manganese, $+2$, $+3$, $+4$, $+6$, and $+7$. In oxidation states of $+2$ and $+3$ both metals form bases and corresponding salts like those of iron. In an oxidation state of $+6$ or $+7$ they form oxygen acids, such as chromic acid (H_2CrO_4) and permanganic acid ($HMnO_4$). In its oxidation state of $+4$ manganese forms an oxide (MnO_2) which is amphoteric. Under reducing conditions all compounds of these elements pass into compounds of lower oxidation states and form salts, while under oxidizing conditions compounds of lower oxidation states are oxidized to compounds of higher oxidation states and form acids. Because of the ease with which these changes take place, compounds of these metals take part in many oxidation-reduction reactions. The oxygen acids of both elements (and their salts) are powerful oxidizing agents.

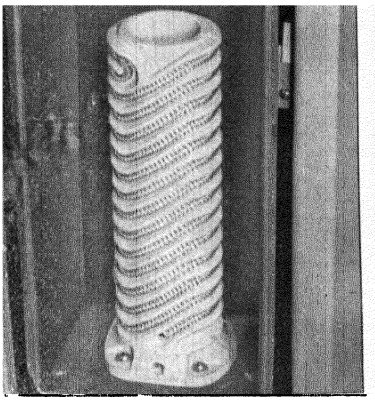
Ores of Chromium and Manganese · While both chromium and manganese are constituents of many minerals, and manganese especially is widely distributed in nature, the chief ore of chromium is chrome iron ore, $Fe(CrO_2)_2$, or $FeO \cdot Cr_2O_3$ (chromite), and that of manganese is the dioxide, MnO_2 (pyrolusite). Both these minerals, as well as other minerals of these metals, are found in various places in the United States, chiefly in Montana, Tennessee, Georgia, and Arkansas, but nearly always in low-grade ores unprofitable to work. We imported in 1953 over 2,227,000 tons of chromite and approximately 3,500,000 tons of pyrolusite. Soviet Russia and regions in Africa, Cuba, and India produce ores of both metals; and in addition Turkey and Greece produce chromite, and Egypt and Brazil pyrolusite.

In recent years methods have been devised for concentrating low-grade manganese ores and for producing from these metallic manganese of high purity by electrolysis. It is hoped that the development of cheap water power in the far Northwest may make the manganese deposits of that region a real industrial source of this much-needed metal.

In a new process, ores containing manganese dioxide are heated to 600° to 900° in a reducing atmosphere, to transform the dioxide into manganese monoxide (MnO), and are then leached with nitric acid. As much as 80 per cent of the manganese can be extracted from low-grade ores available in the United

States. The nitric acid used in the leaching cycle can be recovered at better than 95 per cent.

The Metals · Neither of these metals is used as a pure metal, though both can be prepared by reduction of their oxides by aluminum (p. 605) or by electrolysis of their salts. Pure chromium is *plated* on other metals from baths containing chromic acid together with small concentrations of sulfate or phosphate ions. To secure a good durable plating on iron, the iron is first plated with copper, then with nickel, and finally with chromium. Pure chromium is a very hard, brilliant metal, little affected by air or water, and of melting point about that of iron. Manganese resembles iron in general physical properties, but has a lower melting point (1260°).



Westinghouse Electric Corporation

Fig. 39-1. A Wall-Type Electric Heater · The grille has been removed to show the coils of nickel-chromium resistance wire

Apart from chromium plating, both metals find their greatest use in steel metallurgy. It takes about 15 lb of manganese to make a ton of steel. The metals are prepared for this use in the form of high-percentage iron alloys directly from ores. Chromite gives such an alloy by reduction with carbon:

$$Fe(CrO_2)_2 + 4\,C \longrightarrow Fe + 2\,Cr + 4\,CO\uparrow$$

Manganese ores are mixed with iron ore and the two reduced together. These alloys are called *ferrochromium* and *ferromanganese*. Their use in steel metallurgy and in steel alloys is explained on pages 616 and 619.

Nonferrous Alloys · Both chromium and manganese are constituents of many alloys other than those of iron. Chromium forms many such alloys in various combinations with tungsten, cobalt, molybdenum, vanadium, and copper. Among these are Nichrome and Chromel (nickel and chromium), used for resistance wire in heaters (Fig. 39-1); and Stellite (chromium, cobalt, tungsten), used for making very hard cutting tools and for its rust-resisting properties. In small percentages manganese is a constituent of such alloys as manganese bronze (copper and manganese), used in propeller blades for ships, and Manganin (copper, nickel, manganese), used for wire in standard resistance boxes. Some varieties of brass contain manganese.

Oxides and Hydroxides of the Metals · Both chromium and manganese form oxides corresponding to each of their oxidation states, and in

addition manganese forms the double oxide Mn_3O_4, similar to magnetic oxide of iron (Fe_3O_4). Both metals form hydroxides corresponding to oxides in which the oxidation states of the metals are + 2, + 3, and + 4. Manganese dioxide (MnO_2) (pyrolusite), in which the metal is tetravalent, is the common oxide of manganese, and chromic oxide (Cr_2O_3) is the stable oxide of chromium. It is a bright-green solid, used as a pigment in paints (chrome green) and in the glaze of chinaware, and is made by the reduction of sodium dichromate ($Na_2Cr_2O_7$):

$$Na_2Cr_2O_7 + S \longrightarrow Na_2SO_4 + Cr_2O_3$$

Chromite, containing Cr_2O_3, is used in making heat-resisting bricks for furnace linings.

Salts of Chromium and Manganese as Base-forming Elements · In all common chromium salts chromium acts as a trivalent base and gives salts that are similar to ferric salts in formulas. Crystallized from water, they are all hydrated and are green or violet in color. The deep-violet crystals of potassium chrome alum, $KCr(SO_4)_2 \cdot 12\ H_2O$, are especially well formed. The simple salts are made by the action of acids on chromium oxide or hydroxide,

$$Cr_2O_3 + 6\ HCl \longrightarrow 2\ CrCl_3 + 3\ H_2O$$

or by the action of acids, together with reducing agents, on compounds of higher chromium oxidation state, as will be described in connection with chromates and dichromates.

In the + 4 oxidation state the chemistry of manganese deals largely with manganese dioxide, MnO_2. Manganese dioxide, treated with acids, undergoes reduction and gives salts of bivalent manganese. With hydrochloric acid the primary action seems to be one of ordinary double decomposition:

$$MnO_2 + 4\ HCl \longrightarrow MnCl_4 + 2\ H_2O$$

This is followed by successive reductions of the tetrachloride, with evolution of chlorine:

$$2\ MnCl_4 \longrightarrow 2\ MnCl_3 + Cl_2$$
$$2\ MnCl_3 \longrightarrow 2\ MnCl_2 + Cl_2$$

With concentrated sulfuric acid, manganese sulfate ($MnSO_4$) is formed and oxygen is evolved:

$$2\ MnO_2 + 2\ H_2SO_4 \longrightarrow 2\ MnSO_4 + 2\ H_2O + O_2$$

Manganese dioxide is an excellent catalyst for reactions involving the preparation of oxygen. It is used in the paint and varnish industry to catalyze the absorption of oxygen and thus help to harden the paint. In

the battery industry great quantities of manganese dioxide are used as the oxidizing agent (cathodic material) (p. 223).

In all common salts manganese is bivalent. The soluble ones are always hydrated, such as $MnCl_2 \cdot 4\ H_2O$ and $MnSO_4 \cdot 4\ H_2O$; but the degree of hydration depends on the temperature of crystallization. Sulfates with 5 or 7 molecules of water are easily obtained. All the soluble salts are rose-pink in color; the insoluble ones, such as the carbonate, $MnCO_3$, and the sulfide, MnS, are nearly white.

Preparation of Chromates and Manganates · When a compound of chromium or of manganese is fused with an alkali (or an alkaline carbonate), and with free access of air or with an oxidizing agent, the metals advance to an oxidation state of + 6 and form salts of *acids*. These acids, H_2CrO_4 and H_2MnO_4, are similar to sulfuric acid in formula, and their salts are called *chromates* and *manganates*. With chromium compounds the reactions may be illustrated by the equations

$$2\ Cr_2O_3 + 8\ KOH + 3\ O_2 \longrightarrow 4\ K_2CrO_4 + 4\ H_2O$$
$$4\ Fe(CrO_2)_2 + 16\ KOH + 7\ O_2 \longrightarrow 8\ K_2CrO_4 + 2\ Fe_2O_3 + 8\ H_2O$$

Under similar conditions pyrolusite (MnO_2) yields potassium manganate:

$$2\ MnO_2 + 4\ KOH + O_2 \longrightarrow 2\ K_2MnO_4 + 2\ H_2O$$

The Chromates and Manganates · Potassium chromate (K_2CrO_4) is a well-crystallized, soluble, lemon-yellow salt; and sodium chromate, $Na_2CrO_4 \cdot 10\ H_2O$, is a very soluble yellow salt made by substituting sodium hydroxide (or carbonate) in the reactions just described. Ammonium chromate, $(NH_4)_2CrO_4$, is made by treating chromic acid with a large excess of ammonium hydroxide. It is hydrolyzed by water to form ammonium dichromate, $(NH_4)_2Cr_2O_7$.

Most other chromates are insoluble in water or nearly so. They are yellow, red, or brown in color, and some of them are used as paint pigments. Among these are barium chromate ($BaCrO_4$), zinc chromate ($ZnCrO_4$), and lead chromate ($PbCrO_4$) (chrome yellow). Silver chromate (Ag_2CrO_4) is brick-red in color.

In contrast with the chromates, the manganates are very unstable and exist only in strongly alkaline solutions. From such solutions dark-green crystals of potassium manganate (K_2MnO_4) and sodium manganate ($Na_2MnO_4 \cdot 10\ H_2O$) have been prepared with difficulty. These two salts are isomorphous with the corresponding sulfates.

The Chromate-Dichromate Equilibrium · If we should treat a solution of a chromate with an acid, we might expect to obtain an acid salt:

$$Na_2CrO_4 + H_2SO_4 \longrightarrow NaHSO_4 + NaHCrO_4$$

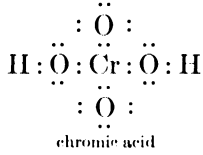
Instead a *di*chromate is formed:

$$2\ Na_2CrO_4 + 2\ H_2SO_4 \longrightarrow 2\ NaHSO_4 + Na_2Cr_2O_7 + H_2O$$

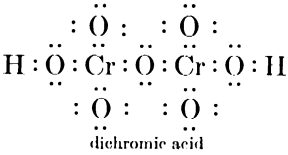
Presumably the dichromate ion is formed by loss of water from the acid chromate ion:

$$2\ HCrO_4^- \longrightarrow H_2O + Cr_2O_7^{--}$$

and dichromic acid is to be considered as a condensed acid (see page 419).



chromic acid



dichromic acid

Addition of a base to the red solution of a dichromate gives the yellow solution of a chromate; while addition of an acid to a yellow chromate solution causes the latter to turn red, indicating the presence of the dichromate ion:

$$Cr_2O_7^{--} + 2\ OH^- \longrightarrow 2\ CrO_4^{--} + H_2O$$
$$2\ CrO_4^{--} + 2\ H^+ \longrightarrow Cr_2O_7^{--} + H_2O$$

It might be thought that some dichromates would be insoluble and capable of preparation by precipitation; but such double decomposition reactions always lead to the precipitation of a *chromate*, not a dichromate:

$$Na_2Cr_2O_7 + 2\ Pb(NO_3)_2 + H_2O \longrightarrow 2\ PbCrO_4\downarrow + 2\ NaNO_3 + 2\ HNO_3$$

The Permanganates · The oxidation state of +7 rather than +6 is the natural maximum oxidation state of manganese; and as we have seen, manganates are stable only in strongly alkaline solutions. If the excess of alkali is neutralized, even by very weak acids, the manganates undergo an interesting hydrolysis, whereby a part of the manganese is oxidized to its more stable oxidation state of +7 at the expense of another part, which is reduced to an oxidation state of +4:

$$3\ K_2MnO_4 + 4\ H_2O \longrightarrow 2\ KMnO_4 + Mn(OH)_4 + 4\ KOH$$

The resulting potassium permanganate ($KMnO_4$) is a salt of permanganic acid ($HMnO_4$). It forms deep-purple soluble crystals, and even its dilute solutions are intensely purple in color. Sodium permanganate crystallizes with difficulty to form hydrated crystals, $NaMnO_4 \cdot 3\ H_2O$. Its solution is used as a disinfectant. All permanganates, like the corresponding perchlorates, are soluble in water.

Permanganates, as well as free permanganic acid, can be prepared by electrolysis of solutions of the manganate under conditions such that the

manganate ions (MnO_4^{--}) are oxidized to permanganate ions (MnO_4^-) at the anode of a suitable cell.

Chromic Acid and Permanganic Acid · These acids are both obtainable from their salts *in dilute solutions*, but neither acid can be crystallized. When concentrated, chromic acid deposits deep purple-red crystals of chromic anhydride (CrO_3),

$$H_2CrO_4 \longrightarrow CrO_3 + H_2O$$

while permanganic acid decomposes into lower oxides of manganese, free oxygen, and water. By carefully treating crystals of potassium permanganate with concentrated sulfuric acid, permanganic anhydride (Mn_2O_7) can be obtained as a highly explosive, greenish, oily liquid.

Oxidizing Action of Chromates, Dichromates, and Permanganates · Chromates, dichromates, and permanganates are strong oxidizing agents, and the reason for this is not difficult to understand. Chromium and manganese are both essentially *metals*, and as such tend to act as simple cations of salts. Under powerful oxidizing conditions they have been pushed into higher oxidation states to form highly oxidized compounds which can be reduced easily. Consequently, in the presence of even mild reducing agents, the chromate and permanganate anions tend to take on electrons and lose their loads of oxygen and pass back to the more natural metallic cations. This reduction of chromates or permanganates may take place either in acid solution, in alkaline solution, or in a neutral one.

Oxidizing Action of Chromates and Dichromates in Acid Solution · In the presence of an acid the chromate ion becomes a dichromate ion which is the oxidizing agent in acid solution. If to an acidified solution of a chromate or a dichromate is added an oxidizable substance, such as ferrous ion, Fe^{++} (easily oxidized to Fe^{+++}), or H_2S (which gives free sulfur on oxidation), a reaction takes place, often quite rapidly.

$$Cr_2O_7^{--} + 14\ H^+ + 6\ Fe^{++} \longrightarrow 2\ Cr^{+++} + 6\ Fe^{+++} + 7\ H_2O$$
$$Cr_2O_7^{--} + 3\ H_2S + 8\ H^+ \longrightarrow 2\ Cr^{+++} + 3\ S + 7\ H_2O$$

The reaction is accompanied by a pronounced color change, since the dichromate ion is red, while the Cr^{+++} ion is dark green (the colors of the Fe^{++} and Fe^{+++} are not intense enough to have much effect).

Oxidizing Action of Permanganates in Acid Solution · In acid solution the manganese in the permanganate ion tends to drop in oxidation state to the cation, Mn^{++}. If an oxidizable substance such as oxalic acid ($H_2C_2O_4$) is added to an acidified solution of a permanganate, the following reaction occurs:

$$2\ MnO_4^- + 5\ H_2C_2O_4 + 6\ H^+ \longrightarrow 2\ Mn^{++} + 10\ CO_2 + 8\ H_2O$$

A permanganate is intensely colored in solution, while the products formed both from the permanganate and from the oxidation of the reducing agent have very little color as a rule. The end point of a reaction in which a permanganate is used as an oxidizing agent is sharply marked by the disappearance of color, which makes potassium permanganate an invaluable reagent in chemical analysis.

Oxidizing Action of Chromates in Neutral or Alkaline Solution · The only difference between the action of chromates in acid solution and in basic or neutral solution is that the chromic ion, Cr^{+++}, is formed in acid solution and chromium hydroxide in basic solution. Thus if a solution of a ferrous salt were made alkaline (in which case ferrous hydroxide would be precipitated) and a solution of a chromate were added, the following reaction would occur:

$$CrO_4^{--} + 3\ Fe(OH)_2 + 4\ H_2O \longrightarrow 3\ Fe(OH)_3 + Cr(OH)_3 + 2\ OH^-$$

Oxidizing Action of Permanganates in Neutral or Alkaline Solutions · In the presence of an oxidizable substance and in neutral or alkaline solution the oxidation state of manganese drops only to +4, and the product formed is $Mn(OH)_4$, or its dehydration product, MnO_2. The reason this occurs appears to be associated with the very low solubility of these substances. For example, alcohol is oxidized, in dilute neutral solution, to acetate ion, $C_2H_3O_2^-$:

$$4\ MnO_4^- + 3\ C_2H_5OH + 4\ H_2O \longrightarrow 4\ Mn(OH)_4 + 3\ C_2H_3O_2^- + OH$$

Rhenium · In 1925, after prolonged search, Walter Noddack and Ida Tacke (at Berlin) announced the discovery of the element of atomic number 75. It was first found by Moseley's X-ray method in ores of tantalum and later in those of molybdenum and manganese. It was named *rhenium* in honor of a German province. Rhenium is available as a rather rare metal of about 400 lb annual production. In chemical properties it resembles manganese. Its density is about 21, and its melting point about 3400°.

Technetium · The element of atomic number 43 was originally called masurium, but the claims of the discovery that led to that name have been disproved. In 1937 element 43 was found in the product of the bombardment of molybdenum with deuterons. Its name is derived from the Greek word for "artificial." It has since been found in relatively large amounts in the fission products of uranium (Chap. 21). The physical and chemical properties of technetium are being studied.

Metallo-acid Elements Used Chiefly as Metals or Alloys

General · Of the remaining five elements in the table at the beginning of this chapter, vanadium forms salts in its lower oxidation states and acids in its higher ones, just as do chromium, manganese, and rhenium. The others, niobium, tantalum, molybdenum, and tungsten, have almost no salt-forming ability as positive ions, but in their higher oxidation states they all form acids. All five form a variety of oxides and compounds with the halogen elements, especially with fluorine and chlorine. All five have high melting points and densities, together with other properties that characterize most heavy metals. They are used chiefly in the form of free metals or alloys, and their compounds do not require special descriptions. They are difficult to prepare in pure form.

Vanadium, Niobium, Tantalum · These three elements constitute family *A*, Group V, in the periodic table, and in their properties show many of the gradations we expect to find in a periodic family.

Vanadium · Vanadium was first described as a new element by Sefstrom in 1830, and named in honor of Vanadis, the Scandinavian goddess of fortune. It is widely distributed in nature but rarely in rich deposits. In the United States the deposits are in Colorado, Arizona, and Utah, and the chief ore is *carnotite*—a complex mineral of the formula $K_2O \cdot 2\,UO_3 \cdot V_2O_5 \cdot 3\,H_2O$. The chief foreign producing countries are Mexico, Peru, and Africa. The Peruvian ore is *patronite*, a complex sulfide, which is mined in the very high Andes Mountains. This mineral seems to be the residue of the complete evaporation of asphalt; and it is of interest that the ashes of nearly all anthracite and of petroleum contain vanadium oxide, sometimes in large percentages.

The Metal · Metallic vanadium is difficult to prepare and has no special uses. It is very hard, rather brittle, and has a brilliant luster. By reducing a mixture of the oxides of iron and vanadium, an alloy called *ferrovanadium* is obtained, which usually contains from 25 to 50 per cent vanadium. It is important in the manufacture of vanadium steel, which is the chief use of vanadium. Some vanadium compounds are employed as catalysts in the manufacture of dyes and especially in the contact process for sulfuric acid (p. 383). For the latter purpose vanadium oxide (V_2O_5) is interspersed throughout some inert porous material, and the product so formed is often called "vanadium mass."

Niobium and Tantalum · The history of these two elements is an interesting story of confused identity. At some early date Governor John

Winthrop sent a specimen of a new mineral found in Connecticut to England, where it became lodged in the British Museum. The mineral was named *columbite* in honor of America. In 1801 the English chemist Hatchett examined this mineral and from it isolated what was undoubtedly the oxide of a new element, which he named *columbium*. A few years later the Swedish chemist Ekeberg examined a Swedish mineral (now called *tantalite*) and found an oxide of a metal which he named *tantalum* (from the Greek mythological figure Tantalus). Later chemists considered these two oxides to be identical, though the German Heinrich Rose maintained they were different. He retained the name *tantalum* for the oxide of Ekeberg, but gave the name *niobium* to Hatchett's columbium (Niobe was the daughter of Tantalus). Finally, after some forty years of uncertainty, the French chemist Marignac prepared pure specimens of tantalic and niobic acids and demonstrated their different properties. Hatchett's metal has been called columbium in the United States, but in the year 1949 the name *niobium* was adopted.

The preparation of the pure metals proved to be very difficult. Moissan prepared some impure specimens in his electric furnace, but the first really pure small specimen of niobium was produced in Germany in 1906. The first production of any quantity of both these metals was exhibited by the American chemist Balke in 1929.

The Ores of Niobium and Tantalum · These two metals are found almost wholly as salts of niobic acid ($HNbO_3$) and tantalic acid ($HTaO_3$); and small percentages of such salts are present in a great variety of minerals. The only minerals adapted to the preparation of the metals themselves are *columbite* and *tantalite*. Both these are mixtures of the iron or manganese salts of both acids in varying proportions. With larger percentages of niobic acid the mineral is called columbite; if tantalum predominates, it is tantalite. If a mineral contains the one acid, it almost always contains the other. They are twin metals, always together and very difficult to separate. Tantalite is sought for the production of metallic tantalum, and is found chiefly in Australia and South Dakota; while columbite, nearly free from tantalum, comes from Africa and is used in making *ferrocolumbium*. In either case the ores are not rich and must be concentrated. About $2\frac{1}{2}$ tons of ore must be mined, concentrated, and processed to produce one pound of tantalum.

Metallurgy · The metallurgy of these elements is strikingly different from that of any others which we have considered. By a number of tedious steps the two metals are brought into the form of double fluorides, which differ in formulas, K_2TaF_7 and K_2NbOF_5. Fortunately these com-

pounds differ somewhat in solubility and can be separated by fractional crystallization. The chemically pure salts are then melted and electrolyzed to yield metallic powders, which cannot be melted in the usual way because of the extremely high melting points of the metals. The powders are compressed into rods by great pressure, and, by the heat generated in the rods by their resistance to an electric current, the metallic particles partially weld together. By alternate heating and hammering of the rods a finished metal is produced.

In 1936 a large deposit of columbite, $Fe(NbO_3)_2$, low in tantalum, was found in Africa. From this ore *ferrocolumbium* is made (like ferrochromium) by reducing the treated mineral with carbon in an electric furnace. The product may contain over half its weight of niobium. The principal use of niobium is in certain types of stainless steels—strong, high-temperature-resistant steels employed in making gas turbines, turbosuperchargers and jet-propulsion motors. It is also used in rods for welding stainless steels. Only a few tons of niobium ores are mined in the United States; several hundred tons are imported annually, largely from the Belgian Congo.

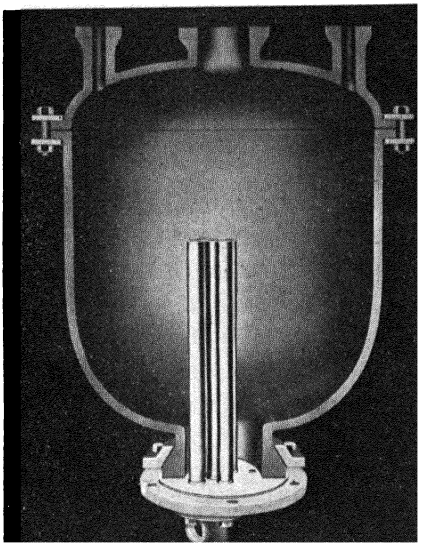
Properties of the Metals · The two metals resemble platinum or polished iron in appearance. Tantalum has a very high melting point, which among metals is second only to that of tungsten; niobium melts at a much lower temperature. Both metals are highly malleable and ductile. In hardness unannealed tantalum is comparable to cold-rolled steel, and the annealed metal to mild steel.

At ordinary temperatures tantalum resists corrosion by nearly all acid and salt solutions. It is most easily attacked by alkalies and by such salts as produce alkalies by hydrolysis. Fluorine attacks it, and it absorbs hydrogen. Niobium is similar to tantalum in many respects, but corrodes more easily and absorbs hydrogen to a greater extent.

Uses of Tantalum · The uses of tantalum depend on its high melting point, hardness, malleability, resistance to corrosion, and its very great heat conductance. These properties lead to its use for many varieties of laboratory articles, for electrodes in radio tubes and in rectifiers (the Balkite rectifier), for nozzles and spinnerets subject to great abrasion, for surgical instruments, and especially for stirrers and steam heaters for corrosive liquids, such as acids and salts (Fig. 39-2, p. 694). Niobium can be used for many of these same purposes.

The oxides of tantalum and niobium, heated with carbon in an electric furnace, yield carbides of great hardness. They can be added to steel to increase its hardness for making cutting tools, or steel tools can be tipped with these carbides. Tantaloy is such a carbide.

Molybdenum and Tungsten · These two elements follow chromium in family *A*, Group VI, of the periodic table. Both the metals, together with chromium, came to the knowledge of chemists in the last two decades of the eighteenth century in the form of definite compounds, but it is within modern times that they have become important as metals.



Fansteel Metallurgical Corporation

Fig. 39-2. Vessel for Heating Corrosive Liquids, Equipped with Tantalum-Tube Heaters

Historical. In 1778 the great Swedish chemist Scheele (Fig 15-1, p 243) became interested in a mineral called *molybdenite*, which had long been confused with graphite. He showed these minerals to be entirely different, and from the molybdenite he isolated an acid oxide which he named molybdic acid, for in those days all acids were thought to be oxides.

Three years later he examined a very heavy, white Swedish mineral, then called tungsten, or heavy stone, now named *scheelite* ($CaWO_4$), and from this he isolated a second acid oxide, WO_3, which he named tungstic acid. A little later this same acid was found in a mineral occurring in Cornish tin mines, which miners called *wolfram*. This led to a confusion of names. The name tungsten is retained for the element in most countries, but the symbol W is universally used to designate it.

Ores of Molybdenum and Tungsten · These two metals (and their compounds) are today produced almost entirely from the minerals in which they were discovered: molybdenum from molybdenite (MoS_2), and tungsten from scheelite ($CaWO_4$) but more largely from wolframite. The latter is a salt of tungstic acid (H_2WO_4) in which the bases consist of iron and manganese in variable proportions, so that the formula is written $(Fe,Mn)WO_4$. Colorado has by far the largest deposit of molybdenite, with smaller ones in California, Canada, and other places. Ores of tungsten have come largely from China and Burma. In the United States wolframite is found in Nevada and Colorado; and scheelite, in California.

Metallurgy of the Metals · Fortunately it is not necessary to extract these two metals from one mineral (as it was with columbium and tantalum), and it is relatively easy by roasting and fusion of ores to work the two metals into the form of the oxides MoO_3 and WO_3. The metals both melt at exceedingly high temperatures; and for their production, espe-

cially for tungsten, it is necessary to resort to "powder metallurgy," as was described in connection with tantalum. The heated oxide is reduced to metallic powder in a current of hydrogen, and the powder is worked into continuous metal, as with tantalum. Molybdic oxide can also be reduced by aluminum.

Properties and Uses of the Metals · In their physical properties the two metals resemble each other closely, though molybdenum melts about 750° lower than tungsten and is approximately half as heavy. Both metals tend to be crystalline and very hard and brittle. By prolonged mechanical treatment they both become very malleable and capable of being drawn into wire much smaller than a human hair. Tungsten is a much better electrical conductor than molybdenum, and the tungsten filament in an electric lamp must be drawn very fine and looped in many loops to have enough resistance to bring the wire to a white heat.

The properties of these metals make them exceedingly useful for all sorts of electrical purposes electrodes, grids, supports in radio and thermionic tubes, electrodes for neon tubes, targets for X-ray tubes, filaments for electric lamps, and contact points for electric switches and automobile distributors. Molybdenum is used chiefly for supporting wires and parts that are not too highly heated, for it is much cheaper than tungsten. Its resistance is greater than that of tungsten, and molybdenum wire is used as the heating unit in some types of electric furnaces. Both metals oxidize easily at higher temperatures and when so used must be protected from air.

A very large use for the metals is in making steel alloys, as described under steel. For this purpose tungsten is prepared as ferrotungsten by the reduction of wolframite with carbon; and ferromolybdenum, by reduction of a mixture of iron oxide and molybdic oxide. Both metals are used in a number of nonferrous alloys as well, chiefly those of chromium, nickel, and cobalt.

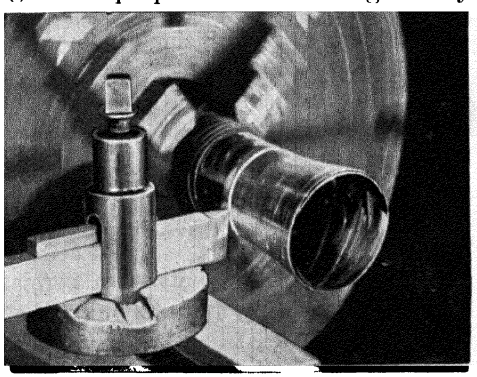


Fig. 39-3. Cutting a Glass Tube with a Carboloy Lathe Tool

Compounds of Molybdenum and Tungsten · Of these the carbides of tungsten are the most interesting, especially the one of the formula WC_2. It is a crystalline material approaching close to the diamond in hardness. It has been found possible to embed these fine crystals in suitable binders,

especially in metallic cobalt, and so obtain a cutting tool that surpasses all others for many uses. Carboloy is the best-known trade name for this material, and a Carboloy lathe tool will cut threads on a hard-glass tube (Fig. 39-3) and can be used to machine hard rubber. The carbides of these metals can also be used as abrasives for grinding hard metal parts.

There are a great many compounds of both molybdenum and tungsten, but few have important useful applications. Both elements form a few simple salts corresponding to chromates, such as K_2MoO_4 and Na_2WO_4; but for the most part the molybdates and tungstates are much more complex and are derived from condensed acids (p. 419). For example, ordinary ammonium molybdate has the formula $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$. Sodium tungstate ($Na_2WO_4$) has some use as a fire-resisting finish on cloth and as a mordant in dyeing. Compounds of molybdenum are used for blue colors in china-painting, for coloring leather, and in dyeing.

QUESTIONS

1. For what reason are the nine elements of this chapter grouped together?

2. Why describe chromium and manganese apart from the other six elements?

3. What distinction can you make between the metallo-elements and those metals whose hydroxides are amphoteric?

4. What six important nonferrous alloys can you name other than those mentioned in this chapter?

5. What chemical principle underlies the production of chromates and manganates from their ores?

6. Why is barium chromate ($BaCrO_4$), rather than barium dichromate, precipitated from an acid solution of sodium dichromate?

7. In the equations on page 689 (*a*) what is oxidized; (*b*) what is reduced; (*c*) what acts as an oxidizing agent; (*d*) what acts as a reducing agent?

8. In hydrochloric acid solution potassium permanganate oxidizes ferrous chloride to ferric chloride. What is the equation?

9. In acid solution sodium dichromate oxidizes methyl alcohol (CH_3OH) to formaldehyde (CH_2O). What is the equation?

PROBLEMS

1. What weight of potassium permanganate can be prepared from 100 g of pure pyrolusite by first preparing the manganate and then treating its solution with nitric acid?

2. In acid solution which salt has the greater oxidizing value per 100 g and by what per cent, potassium permanganate or sodium dichromate?

3. (*a*) What weight of potassium permanganate will be required for the oxidation in alkaline solution of 1 kg of 95 per cent alcohol to acetic acid? (*b*) How could you recover the acetic acid?

4. What weight of (pure) hematite and chromite must be mixed and reduced to obtain 200 lb of ferrochromium containing 50 per cent chromium and 5 per cent carbon?

5. A sample of iron ore weighing 0.3 g was dissolved in sulfuric acid, and the resulting ferrous sulfate was oxidized to ferric sulfate by potassium permanganate. The oxidation required 28 ml of a solution of the permanganate prepared by dissolving 3.16 g of the permanganate in 1 liter of water. Calculate the percentage of iron that was present in the ore.

CHAPTER 40

THE PLATINUM FAMILY

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Ruthenium (Ru) .	101.7	44	12.2	2450° (?)	2, 8, 18, 14, 2
Rhodium (Rh) . .	102.91	45	12.5	1955°	2, 8, 18, 15, 2
Palladium (Pd) . .	106.7	46	12.0	1555°	2, 8, 18, 16, 2
Osmium (Os) . . .	190.2	76	22.48	2700° (?)	2, 8, 18, 32, 14, 2
Iridium (Ir) . . .	193.1	77	22.4	2410°	2, 8, 18, 32, 15, 2
Platinum (Pt) . .	195.23	78	21.45	1755°	2, 8, 18, 32, 16, 2

General · In the same groups as iron, cobalt, and nickel are six other elements (see table below), ruthenium, rhodium, palladium, osmium, iridium, and platinum, which are very closely related to one another and are known collectively as the *platinum metals*. They too are transition elements (periodic table, p. 313); hence we can expect them to form a number of stable complex ions. Indeed, most of their chemistry is that in which they are combined in complexes.

TRANSITION ELEMENTS
(Elements in which inner shells are being filled to 18 or 32 electrons)

45.10 Sc 21	47.90 Ti 22	50.95 V 23	52.01 Cr 24	54.93 Mn 25	55.85 Fe 26	58.94 Co 27	58.69 Ni 28	63.54 Cu 29
88.92 Y 39	91.22 Zr 40	92.91 Nb 41	96.95 Mo 42	Tc 43	101.7 Ru 44	102.91 Rh 45	106.7 Pd 46	107.880 Ag 47
Rare-Earth Elements 57-71	178.6 Hf 72	180.88 Ta 73	183.92 W 74	186.31 Re 75	190.2 Os 76	193.1 Ir 77	195.23 Pt 78	197.2 Au 79
Actinide Series 89——								

Transition Elements

Platinum

History and Occurrence · The element *platinum* owes its name to the Spanish word *platina*, which is a diminutive of the word *plata*, "silver." Platinum was introduced into Europe through the Spanish conquests of Peru and Mexico. The first large quantity reached England in 1740 from Jamaica, and in 1750 it was first described with some care by Brownrigg. It occurs in nature alloyed with the various metals belonging to the platinum family, as well as with other metals. Like gold, it occurs in

heavy sands, associated with magnetite, zircon, diamond, and quartz, and constitutes from 50 to 80 per cent of the crude alloy. A single well-defined mineral compound is known, namely, *sperrylite* ($PtAs_2$). Formerly nearly all the world's supply of platinum came from the Ural Mountains, in Russia. In recent years Canada has been the chief producer, owing to the recovery of platinum from the electrolytic mud of the copper and nickel refineries at Sudbury, Ontario. Russia, South Africa, the United States (Alaska, California, and Oregon), and Colombia are important producers.

Preparation · Native platinum is usually alloyed with gold and the platinum metals in flakes, scales, or small nuggets. To separate the platinum the alloy is dissolved in aqua regia, which converts the platinum into chloroplatinic acid (H_2PtCl_6). Ammonium chloride is then added, which precipitates the platinum as insoluble ammonium chloroplatinate:

$$H_2PtCl_6 + 2\,NH_4Cl \longrightarrow (NH_4)_2PtCl_6\downarrow + 2\,HCl$$

Some iridium is also precipitated as a similar compound. On ignition the chloroplatinate is decomposed, leaving the platinum as a spongy metallic mass, which is melted in an electric furnace and rolled or hammered into the desired shape.

Properties · Platinum is a grayish-white metal which is very malleable and ductile, and is harder than gold. In finely divided form it adsorbs gases and occludes hydrogen. A jet of hydrogen or coal gas directed upon spongy platinum, in air, is at once ignited. Under ordinary conditions it is not attacked by the common acids, though hot concentrated sulfuric acid slowly dissolves it. It is resistant to the action of air, and neither oxygen nor water vapor attacks it even at red heat. Free chlorine dissolves it, forming platinum tetrachloride ($PtCl_4$). Aqua regia converts it into *chloroplatinic acid* (H_2PtCl_6). Fused alkalies corrode it, forming platinates, especially in the presence of oxidizing agents such as nitrates. It alloys readily with many easily reducible metals, and is therefore attacked or dissolved when heated with compounds of such metals together with a reducing agent. Since hydrogen gas readily passes through sheet platinum when the latter is hot, it is not safe to heat, in a gas flame, any easily reducible oxide in a platinum crucible.

Platinum as a Catalytic Agent · Platinum is remarkable for its property of acting as a catalytic agent in a large number of chemical reactions, and mention has been made of this use of the metal in connection with the manufacture of sulfuric acid (p. 383). The catalyst support, generally some porous or fibrous substance, such as asbestos, is soaked in a solution of chloroplatinic acid and then ignited. The platinum compound is decomposed, and the platinum deposited in very finely divided form. Asbestos prepared in this way is called *platinized as-*

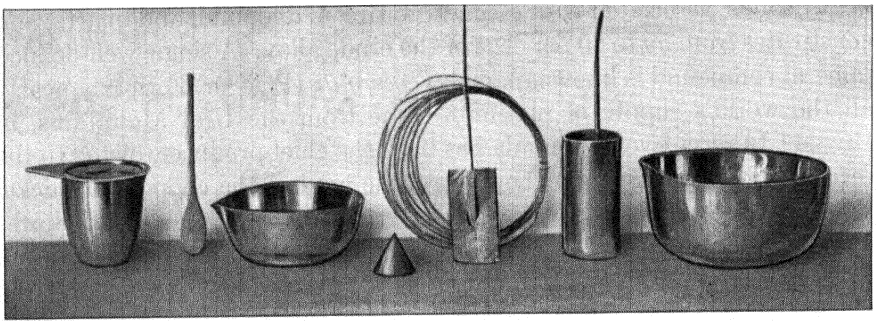


Fig. 40-1. Platinum Utensils Used in Chemical Laboratories

bestos. For some reactions, as in the oxidation of ammonia by air (p 402), the platinum is used in the form of a finely woven gauze. The catalytic action seems to be in part connected with the property of adsorbing gases and rendering them nascent.

Applications · Platinum is more costly than gold, but its value is subject to wide fluctuations. Its applications are therefore limited. Its greatest use is in the making of jewelry; more than one half of the supply is used for this purpose. Next in order comes its use for chemical and dental purposes. Smaller amounts are used (1) in the construction of electric apparatus, (2) as a catalyst in certain industrial processes, and (3) for making crucibles and evaporating dishes used in scientific laboratories (Fig. 40-1).

Platinum Substitutes · To conserve the limited supply of platinum, efforts have been made to provide substitutes for some of its uses. Tungsten is taking its place for many purposes, especially for electrical spark contacts; tantalum can replace it in making many scientific instruments; wires of nickel-iron coated with copper are now used as lead-in wires in incandescent lamps; electrical-resistance heaters are made of alloys of nickel and chromium; quartz dishes are substituted for platinum in the industries; and a variety of alloys such as *Palau*, an alloy of palladium and gold, have been proposed for use in small laboratory utensils, though none has any very wide application.

Compounds of Platinum · Like tin, platinum acts either as a bivalent or as a tetravalent element, and the hydroxide corresponding to each oxidation state can act either as an acid or as a base. Some trivalent compounds are also known. In general, the oxygen derivatives of platinum, including the oxygen acids, as well as the platinates and platinites, are unstable and easily decomposed by heat. Its best-known compounds are its halogen derivatives, especially the salts of *chloroplatinic acid* (H_2PtCl_6). This free acid, which forms reddish, deliquescent crystals of the composi-

tion $H_2PtCl_6 \cdot 6\ H_2O$, is obtained by dissolving platinum in aqua regia. When added to a solution of potassium chloride, *potassium chloroplatinate* is formed as a reddish-yellow salt:

$$H_2PtCl_6 + 2\ KCl \longrightarrow K_2PtCl_6\downarrow + 2\ HCl$$

Sodium chloride and ammonium chloride act in the same way. The sodium salt, however, is soluble in dilute alcohol, while the salts of potassium and ammonium are not, and this difference in property is taken advantage of in the separation of potassium and sodium from each other.

Palladium, Rhodium, Ruthenium, Osmium, and Iridium

These other platinum metals are all gray metals and have very high melting points and densities. They are found alloyed with native platinum. In chemical conduct they are like gold and platinum. Each one forms several series of compounds, in which the oxidation state is either $+2$, $+3$, or $+4$; each gives a variety of oxygen compounds of rather unstable character.

Palladium · Palladium is the most abundant one of the five. It is obtained from native platinum and also from the electrolytic muds that result from the refining of certain nickel ores, especially those at Sudbury, Ontario. It is a soft metal, closely resembling platinum in appearance, but of less density and of lower melting point. It is more pronouncedly basic than the others, dissolves in concentrated acids, especially in nitric acid, and forms a number of bivalent and moderately stable salts, such as the nitrate, $Pd(NO_3)_2$, and the sulfate, $PdSO_4$. The metal has the remarkable property of occluding, or absorbing, a very large volume of hydrogen. This may amount to as much as 800–900 times the volume of the palladium, and an even larger volume is absorbed when an electrode is covered with the spongy metal and is made the cathode in the electrolysis of a dilute acid solution. The hydrogen so absorbed is in a very active state, showing the reactions appropriate to its position in the electrochemical series. For example, palladium thus charged with hydrogen, when dipped into a solution of copper salt, at once precipitates copper.

Palladium is used in making delicate instruments, and as a substitute for platinum in jewelry. It is not only cheaper than platinum, but only about half as dense, so that a given weight will go twice as far. It is used also as a catalyst in industrial reactions.

Rhodium · Rhodium resembles aluminum in appearance. It is used to some extent in plating jewelry. Of the metals in the platinum family, it is the most easily attacked by free chlorine; but it is exceedingly resistant to the action of acids. Its salts are rose-colored.

Ruthenium · Ruthenium is hard and brittle, and closely resembles platinum in appearance. It forms a variety of oxygen compounds, the formulas of which recall those of manganese—for example, RuO_2, K_2RuO_4, and $KRuO_4$. It also forms a volatile oxide of the formula RuO_4. This is produced by the oxidizing action of aqua regia, and is possibly formed by heating the metal in the air. It is a yellow compound, which melts at 25.5°.

Osmium · Of all known substances, osmium has the greatest density (22.48). It is very hard and infusible. It is acted upon by aqua regia to form an oxide, OsO_4, which resembles the corresponding oxide of ruthenium. This oxide is volatile with steam and is often present in the steam arising when solutions of crude platinum salts are boiled. It has a very irritating and unpleasant odor, and is called *osmic acid*, though it has no acid properties, nor does it form an acid with water. It is characterized by a very strong corrosive action, which it owes to oxidizing properties, not to acid properties. In acting as an oxidizing agent it deposits metallic osmium in very finely divided form, and this is a great irritant when deposited in sensitive tissues. It is used in biological laboratories as a hardening agent and as a stain in the preparation of microscopic sections.

Iridium · This element owes its name to the variety of colors seen during its chemical transformations. It is a silver-white metal, hard and brittle. It is often present in the platinum of laboratory vessels, making the latter harder and less subject to chemical corrosion. The standard meter bar preserved at Sèvres is an alloy of platinum and iridium. The residue obtained when native platinum is digested with aqua regia is essentially an alloy of iridium and osmium. It can be worked up into a very hard alloy called *iridosmine* (found also as a natural alloy), which is used as a material for pointing gold pens. It is produced in very limited quantities and is more expensive than gold.

QUESTIONS

1. What metal has (*a*) the greatest density; (*b*) the least density; (*c*) the highest melting point; (*d*) the lowest melting point; (*e*) the highest atomic weight; (*f*) the lowest atomic weight?

2. What metals are not attacked by any of the common acids?

3. What properties of platinum make it useful (*a*) as a catalyst; (*b*) in the manufacture of jewelry; (*c*) in the construction of laboratory vessels?

4. What is the chemistry involved in the separation and purification of native platinum?

5. What method, involving a compound of platinum, may be used to separate sodium ions from potassium ions?

6. (*a*) Write the equation for the ionization of chloroplatinic acid. (*b*) What is the valence of the anion? (*c*) To what class of ions does the anion belong?

7. How could platinum be distinguished from white gold (*a*) by physical means; (*b*) by chemical test?

PROBLEMS

1. Calculate the per cent of platinum (*a*) in 10 g of platinic chloride; (*b*) in 10 g of chloroplatinic acid.

2. A sample of a platinum alloy weighing 0.2000 g was dissolved in aqua regia, and the platinum was precipitated as potassium chloroplatinate; the precipitate weighed 0.0996 g. What was the per cent of platinum in the alloy?

CHAPTER 41

COPPER, SILVER, AND GOLD

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Copper (Cu)	63.57	29	8.92	1083°	2, 8, 18, 1
Silver (Ag)	107.88	47	10.5	960.5°	2, 8, 18, 18, 1
Gold (Au)	197.2	79	19.3	1063°	2, 8, 18, 32, 18, 1

General · The elements copper (Cu), silver (Ag), and gold (Au) are often called the coinage metals because of their long use in coins and for barter. They are "noble" metals; that is, they are relatively inactive and do not show any pronounced tendency to give up electrons to become ions. They are, as a result, found free in nature.

The oxides, Cu_2O, Ag_2O, and Au_2O, are only weakly basic. The free elements are dense. They have, in addition to the oxidation state of + 1, corresponding to a loss of a single valence electron, higher oxidation states which involve the loss of one or more electrons from the shell below the outer, or valence, shell. The ions of copper, silver, and gold possess the property of forming stable complexes, such as $Cu(NH_3)_4^{++}$, $Cu(H_2O)_4^{++}$, $Ag(NH_3)_2^{+}$, and $AuCl_4^{-}$.

Many of these properties can be correlated with the fact that copper, silver, and gold are transition elements. In fact, they are the last elements in the three transition series, and are the elements whose atoms have just filled an inner shell to 18 electrons.

TRANSITION ELEMENTS
(Elements in which inner shells are being filled to 18 or 32 electrons)

45.10 **Sc** 21	47.90 **Ti** 22	50.95 **V** 23	52.01 **Cr** 24	54.93 **Mn** 25	55.85 **Fe** 26	58.94 **Co** 27	58.69 **Ni** 28	63.54 **Cu** 29
88.92 **Y** 39	91.22 **Zr** 40	92.91 **Nb** 41	96.95 **Mo** 42	**Tc** 43	101.7 **Ru** 44	102.91 **Rh** 45	106.7 **Pd** 46	107.880 **Ag** 47
Rare-Earth Elements 57-71	178.6 **Hf** 72	180.88 **Ta** 73	183.92 **W** 74	186.31 **Re** 75	190.2 **Os** 76	193.1 **Ir** 77	195.23 **Pt** 78	197.2 **Au** 79
Actinide Series 89—								

Transition Elements in Which an Electron Shell of 8 Is Being Filled to 18 or 32

Copper

Occurrence · Metallic copper has been known from the earliest times and was probably the first metal to come into any considerable use. This is explained by its native occurrence in large pieces and by the ease with which its oxygen compounds are reduced. Well-fashioned copper articles have been found that are at least six thousand years old. The metal owes its name (from the Latin word *cuprum*) to the fact that the Romans obtained it from the island of Cyprus.

Large quantities of native copper, in a state approximating purity, are found in the northern peninsula of Michigan, and smaller deposits are found in other localities. In combination copper is found in a wide variety of forms, especially as sulfides, oxides, carbonates, and silicates. In small quantities it is present in the great majority of sulfide minerals, and in traces it is very widely distributed in nature. To some extent it is absorbed by plants growing in copper-bearing regions. Traces of copper are found in the human body.

Ores of Copper · The table which follows gives a list of the most important ores, chalcopyrite being by far the most valuable. Much copper is also produced from impure native copper.

SOME ORES OF COPPER	SULFIDE ORES		OXYGEN ORES	
	Chalcopyrite	$CuFeS_2$	Cuprite . . .	Cu_2O
	Chalcocite	Cu_2S	Melaconite .	CuO
	Bornite	Cu_5FeS_4	Malachite . .	$CuCO_3 \cdot Cu(OH)_2$

Nearly all countries produce some copper. Chile probably has the largest single deposit yet discovered; but the United States produces over a quarter, and North America nearly half, of the world's normal production, which totals about 3,000,000 tons annually. The chief copper-producing areas are Alaska, Montana, Utah, and Michigan.

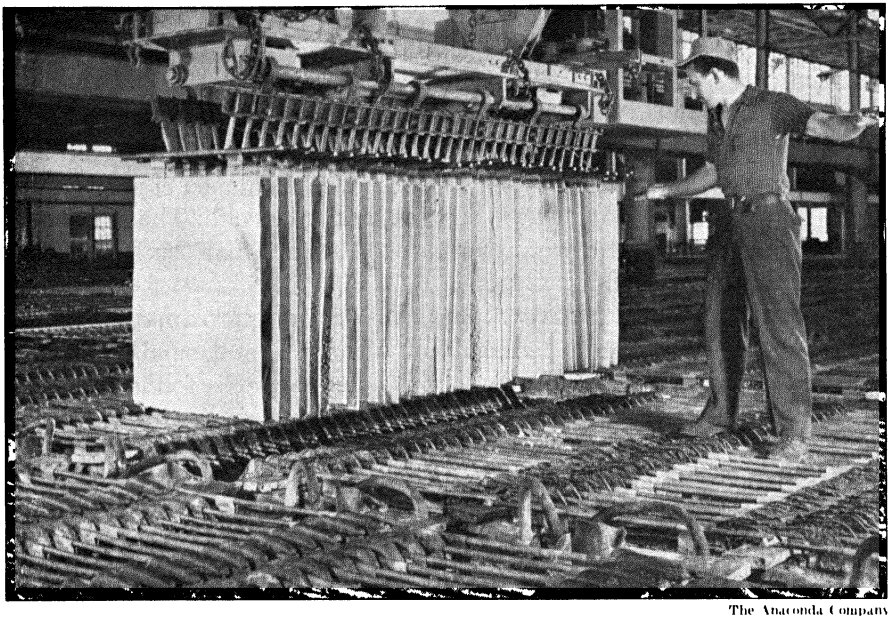
Metallurgy · Two general methods are used to separate copper from its ores:

1. **Leaching method.** This method consists in treating the ore with some reagent, such as dilute sulfuric acid or ammonium hydroxide, that will dissolve the copper. This method is, of course, applicable only when the copper is present in a form, such as the carbonate or oxide, which is soluble in the reagent employed.

$$CuCO_3 \cdot Cu(OH)_2 + 2\ H_2SO_4 \longrightarrow 2\ CuSO_4 + 3\ H_2O + CO_2 \uparrow$$

From the leaching solution the copper may be obtained by electrolysis or by precipitation with another metal:

$$CuSO_4 + Fe \longrightarrow Cu \downarrow + FeSO_4$$



The Anaconda Company

Fig. 41-1. View in an Electrolytic Copper Refinery: Withdrawing the Pure Copper Cathodes from the Cells

2 **Smelting, or pyrometallurgical, method.** In this method the copper ore (usually copper sulfides, mixed or combined with other metallic sulfides, especially iron, as well as with small amounts of gold and silver) is heated with an appropriate flux in a blast furnace (p. 611) or reverberatory furnace, much like the open hearth furnace (p. 615). The sulfides of copper and iron melt, and the resulting liquid (known as *matte*) is separated from the slag and is poured into especially designed Bessemer converters. Any gold and silver present in the original ore is in solution in the liquid matte. Air is forced through the converter, and silica is then added. A certain percentage of the sulfides is changed into oxides by the process. The iron oxide combines with the silica, forming a slag that can be poured off, while the copper oxide reacts with some unchanged copper sulfide, as follows.

$$2\,Cu_2O + Cu_2S \longrightarrow 6\,Cu + SO_2\uparrow$$

The resulting copper, which contains any gold or silver present in the ore, when cast in molds, is known as *blister copper*. This generally contains less than 3 per cent of impurities.

Refining of Copper · Almost always blister copper is refined in order to recover the precious metals dissolved in it. For refining, the liquid metal from the converter is charged onto the hearth of a reverberatory refining furnace resembling an open-hearth steel furnace. The impurities are oxidized and pass into a slag, but the gold and silver are not affected. The purified copper is then cast into anode plates weighing as much as 300 lb each. These are suspended in an electrolyte of copper sulfate and free sulfuric acid, and the anode copper is de-

posited upon a cathode of pure sheet copper. The gold and silver collect in the mud at the bottom of the electrolytic cells, and this is worked over to obtain the precious metals.

Properties of Copper · Copper is a heavy metal of characteristic ruddy color. It is rather soft and is very ductile, malleable, and flexible, yet tough and fairly strong. As an electrical conductor it is second only to silver. It is not attacked by nonoxidizing acids (unless oxygen is present) or by fused alkalies, but oxidizing acids convert it into the corresponding salts. In the presence of air most acids slowly act upon it; even carbon dioxide in moist air gradually covers its surface with a greenish coating of a basic carbonate. When heated in the air, it is oxidized to black copper oxide (CuO). Sulfur and the halogens attack it much more readily than does oxygen.

Uses of Copper · About one fourth of all the copper produced is used for electrical purposes. Such copper must be exceedingly pure, since even minute quantities of impurities, especially arsenic, greatly diminish the electrical conductivity of the metal. The copper wire in telephone service alone would reach farther than the distance from the earth to the sun. Less pure copper has a wide use as a noncorrosive metal for roofing, for outside trim, for coppering the bottoms of ships, and for a wide range of factory and domestic utensils; it is also used for electrotyping.

A second very great use of copper is in the making of alloys. More than a thousand varieties of these alloys are recognized commercially, and the more familiar names, such as *brass* and *bronze*, now indicate merely the *type* of the alloy, since their composition is subject to wide variation. Some alloys, however, have rather definite compositions. Examples of each are given in the table on page 708.

Simple Compounds of Copper · Copper forms two series of simple salts, derived from the oxides Cu_2O and CuO, known respectively as the *cuprous salts* and the *cupric salts*. Under ordinary conditions, in the presence of moisture and air, the cupric compounds are much the more stable, while at high temperatures cuprous compounds are the stable form. The aqueous solutions of cupric compounds are blue, while cuprous compounds are usually insoluble or give colorless solutions. Both cuprous hydroxide (CuOH) and cupric hydroxide ($Cu(OH)_2$) are rather weak bases, and their salts are somewhat hydrolyzed in solution, giving the solution an acid reaction. They also form many basic salts, which are very sparingly soluble. All copper salts are more or less poisonous, especially to lower forms of life, and a number of them are used as insecticides and fungicides (see Bordeaux mixture, p. 710, and Paris green, p. 782).

SOME ALLOYS OF COPPER

Variable Copper Alloys

(The elements other than copper are given in the order of their percentages.)

CLASS	COMPONENTS	CLASS	COMPONENTS
Simple brasses	Cu, Zn	Ordinary bronze	Cu, Sn
Leaded brasses	Cu, Zn, Pb	Phosphor bronze	Cu, Sn, P
Tin brasses	Cu, Zn, Sn	Zinc bronze	Cu, Sn, Zn, (P)
Leaded tin brasses	Cu, Zn, Sn, Pb	Leaded zinc bronze	Cu, Sn, Zn, Pb
High-tensile brasses	Cu, Zn, Al Cu, Zn, Fe	Lead bronze	Cu, Sn, Pb, (Zn) Cu, Pb, Sn, (Zn)
Manganese brasses	Cu, Zn, Mn Cu, Mn, Zn	Special bronze (X = any metal)	Cu, Sn, X
Nickel silver (German silver)	Cu, Ni, Zn Cu, Zn, Ni	Aluminum bronze	Cu, Al Cu, Al, (Fe, Mg, Mn, Ni, Pb, Si)
Beryllium copper	Cu, Be		

Constant Copper Alloys

NAME	PERCENTAGE COMPOSITION
18-carat gold	Gold, 75%; copper, silver
14-carat gold	Gold, 58%; copper, silver
Gold coin	Gold, 90%; copper, 10%
Silver coin	Silver, 90%; copper, 10%
Nickel coin	Copper, 75%; nickel, 25%
Sterling silver	Silver, 92.5%; copper, 7.5%

Cuprous Compounds · Cuprous salts are rarely derived from oxygen acids, but are represented by such compounds as the oxide, sulfide, cyanide, and the halides. They are prepared in two general ways:

1. **By heating a solution of a cupric salt with a reducing agent.** The simplest reactions of this kind are those in which metallic copper is employed as the reducing agent. The preparation of cuprous chloride is an example:

$$CuCl_2 + Cu \longrightarrow 2\,CuCl$$

2. **By the dissociation of cupric compounds.** At higher temperatures most binary cupric compounds dissociate to form cuprous compounds:

$$4\,CuO \longrightarrow 2\,Cu_2O + O_2\uparrow$$
$$2\,CuS \longrightarrow Cu_2S + S\uparrow$$

Cuprous compounds are nearly all very sparingly soluble in water and are strong reducing agents, tending to pass into cupric salts.

Cuprous Oxide (Cu_2O) · Cuprous oxide is found in nature as a deep-red mineral called *ruby copper* or *cuprite*. It is formed as a precipitate when cupric compounds are heated with a reducing agent in alkaline solution. Cupric hydroxide is first formed, and this is then reduced as follows:

$$2\,e^- + 2\,Cu^{++} + 2\,OH^- \longrightarrow Cu_2O + H_2O$$

Certain sugars in solution effect this reduction, and the formation of cuprous oxide is often employed as a test for these. As a colloidal dispersion, cuprous oxide imparts a ruby-red color to glass.

***Cuprous Sulfide* (Cu_2S)** · This compound is found in nature as a dark-gray mineral called *chalcocite*. It is formed when cupric sulfide is heated in the absence of air, preferably in a current of hydrogen:

$$2\,CuS + H_2 \longrightarrow Cu_2S + H_2S$$

***Cuprous Chloride* ($CuCl$)** · Cuprous chloride is a snow-white crystalline solid, almost insoluble in water. It is most easily prepared by heating a solution of cupric chloride with copper turnings, or by passing a current of sulfur dioxide into a hot solution of a cupric salt and hydrochloric acid:

$$2\,CuSO_4 + 2\,HCl + 2\,H_2O + SO_2 \longrightarrow 2\,CuCl + 3\,H_2SO_4$$

It is readily soluble in concentrated hydrochloric acid and in ammonia water, in both cases forming complex compounds. These solutions absorb many gases, especially oxygen, carbon monoxide, and acetylene. With acetylene, a chocolate-colored precipitate of cuprous acetylide is formed:

$$2\,CuCl + C_2H_2 + 2\,NH_3 \longrightarrow Cu_2C_2 + 2\,NH_4Cl$$

With carbon monoxide an addition product is formed:

$$CuCl + CO + H_2O \longrightarrow CuCl \cdot CO \cdot H_2O$$

One of the methods used for determining the percentages of these two gases present in gas mixtures is based upon these reactions.

***Cuprous Cyanide* ($CuCN$)** · This white insoluble salt is formed by a reaction that might be expected to yield *cupric* cyanide; but the latter compound spontaneously decomposes into the *cuprous* salt and cyanogen:

$$2\,CuSO_4 + 4\,KCN \longrightarrow 2\,K_2SO_4 + 2\,CuCN + C_2N_2\uparrow$$

Cupric Compounds · The cupric salts are the familiar salts of copper. In most cases they are obtained by the usual methods, and a great variety of them are known, both normal and basic. In the solid state they are usually blue, green, or yellow; in dilute solution they are all blue. Some of them can be employed as mild oxidizing agents, being converted into cuprous compounds. Only a few require detailed description.

***Cupric Oxide* (CuO)** · The black oxide of copper is usually obtained commercially by heating copper powder or turnings in air. It is insoluble in water, but is readily soluble in acids, yielding the corresponding salts. Owing to the ease with which it gives up its oxygen, it is a good oxidizing agent and finds extensive use in the laboratory for such operations as the quantitative oxidation of carbon compounds.

***Cupric Hydroxide* ($Cu(OH)_2$)** · The insoluble hydroxide results as a pale-blue colloidal precipitate when any cupric salt is brought together with a solution of a metallic base:

$$CuSO_4 + 2\,KOH \longrightarrow K_2SO_4 + Cu(OH)_2\downarrow$$

When the mixture is boiled, the hydroxide is converted into the oxide:

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$

***Cupric Sulfide* (*CuS*)** · Cupric sulfide results as a brownish-black precipitate when a solution of a cupric salt is treated with hydrogen sulfide:

$$CuSO_4 + H_2S \longrightarrow CuS\downarrow + H_2SO_4$$

It is insoluble both in water and in dilute acids. It is also nearly insoluble in a solution of ammonium sulfide, which distinguishes it from some other sulfides.

***Cupric Sulfate* (*$CuSO_4$*)** · In its industrial uses cupric sulfate is the most important of the salts of copper. Under ordinary conditions it crystallizes from solution in blue triclinic crystals, often of very large size, having the composition $CuSO_4 \cdot 5\,H_2O$ and known as *blue vitriol* or bluestone. A number of other hydrates are known, all of which, when strongly heated, yield the anhydrous salt, which is white. In the industries it is obtained in the refining of silver (p. 713) and by the oxidation of pyrite containing copper:

$$CuS + 2\,O_2 \longrightarrow CuSO_4$$

Prepared in these ways it contains a considerable percentage of ferrous sulfate as an impurity. It is used as a source of copper in the manufacture of other copper salts; as an electrolyte in copper refining, in electrotyping, and in batteries; and for the treatment of hoof diseases, particularly in sheep. A solution containing cupric sulfate, potassium sodium tartrate, and sodium hydroxide is known as *Fehling's solution* and is used in the detection of certain sugars. The insecticide known as *Bordeaux mixture* is made by adding calcium hydroxide to a cold solution of copper sulfate. Many lower organisms, particularly those known as algae, are destroyed by even traces of soluble copper salts, and copper sulfate is sometimes added to the water supply of cities to kill the algae, whose growth gives an unpleasant taste and odor to the water.

Cupric Carbonate · The normal carbonate of copper is not known, but there are a number of basic carbonates, the chief of which are $CuCO_3 \cdot Cu(OH)_2$ and $Cu(OH)_2 \cdot 2\,CuCO_3$. Both of these occur in nature, the former as the green mineral *malachite*, and the latter as the blue mineral *azurite*. The green color of weathered copper is due to the formation of basic carbonates.

Other Cupric Salts · Among the other cupric salts frequently used in the laboratory are the following, most of which form other hydrates in addition to those given:

Cupric nitrate ($Cu(NO_3)_2 \cdot 6\ H_2O$), blue deliquescent crystals.
Cupric chloride ($CuCl_2 \cdot 2\ H_2O$), light-blue pearly scales, or needles.
Cupric bromide ($CuBr_2$), brownish-purple crystals resembling iodine.
Cupric acetate ($Cu(C_2H_3O_2)_2 \cdot H_2O$), a blue easily crystallized salt.

Complex Salts of Copper · Like nearly all the metals of high density, copper forms a great many double and complex salts. Only two general classes will be mentioned here; these are of importance in themselves and represent classes which will frequently recur with other metals.

1. **Ammonia compounds.** When cupric sulfate is treated with aqua ammonia, the insoluble hydroxide is at first precipitated, as would be expected. Continued addition of ammonia causes the precipitate to dissolve, forming an intensely blue-purple solution. From this solution, under favorable conditions, there crystallizes a solid of the same intense color, which has the formula $Cu(NH_3)_4SO_4 \cdot H_2O$. Most cupric salts, even insoluble ones, yield similar compounds with excess of ammonia, and all have the same intense color, quite unlike the pale blue of simple copper salts. The copper ion of copper hydroxide combines with *ammonia* to form the complex ion $Cu(NH_3)_4^{++}$, which from concentrated solutions forms crystals with the sulfate ion SO_4^{--}:

$$Cu(NH_3)_4^{++} + SO_4^{--} \rightleftarrows Cu(NH_3)_4SO_4$$

Salts of this kind, containing ammonia molecules as a constituent of the cation, are called *ammines*, the salt just described being *tetrammine copper* (II) *sulfate*. The dissolving of a precipitate by continued addition of the reagent which produced it may usually be taken to indicate the formation of a complex ion of this general kind.

Under similar circumstances cuprous compounds yield colorless compounds in which there are usually two ammonia groups. Thus diammine copper (I) chloride has the formula $Cu(NH_3)_2Cl$.

2. **Complex cyanides.** We have seen that when a cupric salt and a soluble cyanide are brought together in solution, insoluble cuprous cyanide (CuCN) is formed. If an excess of the cyanide is added, the precipitate dissolves, and the resulting solution is colorless. When treated with the reagents which usually precipitate copper compounds (for example, with hydrogen sulfide), it gives no precipitate, nor does it turn blue-purple with ammonia. These facts point to the formation of a complex ion, and experiment shows that the product is a complex cyanide. Several different cyanides may form, depending upon conditions, a typical one having the formula $KCu(CN)_2$ and containing the ion $Cu(CN)_2^-$. The copper has become a part of a complex anion, and only to an extremely limited extent are simple cuprous ions formed by the reactions

$$Cu(CN)_2^- \rightleftarrows CuCN + CN^- \rightleftarrows Cu^+ + 2\ CN^-$$

Silver

History and Occurrence · Silver, the *argentum* of the Romans, has been known from the earliest times and, together with gold, has always ranked as a precious metal. It is frequently found native, embedded in primitive rock, in the form of flakes or wire and occasionally in large masses. In the combined state it occurs in many minerals, those of most importance to the metallurgist being the following: *cerargyrite* (horn silver) ($AgCl$), *argentite* (Ag_2S), *proustite* (Ag_3AsS_3), *pyrargyrite* (Ag_3SbS_3), *stephanite* ($(Ag_2S)_5 \cdot Sb_2S_3$). It is found also in small quantities in practically all copper and lead ores. A considerable quantity of the silver now produced comes from this source.

Mexico is the largest producer of silver; the United States comes second. The principal silver-producing states are Idaho, Utah, Arizona, and Montana, in the order given. In more recent years the value of silver has greatly declined, and its production has correspondingly diminished, to about 38,000,000 troy ounces per year.

Properties of Silver · Silver is a heavy, rather soft, white metal, very ductile and malleable, and capable of taking a high polish. It melts at 960.5° (a little lower than copper). It surpasses all other metals as a conductor of heat and electricity, but is too costly to find extensive use for such purposes. It alloys readily with other heavy metals, and when it is to be used for coinage or for tableware a small quantity of copper —from 7.5 per cent to 10 per cent— is melted with it to give it hardness (sterling silver) (p. 708).

Metallurgy · In a text of this scope it is possible to explain only the most general principles of the metallurgy of silver, since the details are very complicated and subject to frequent change. The two methods commonly employed are *smelting* and *hydrometallurgy*.

1. **Smelting.** In furnace smelting, the ores are mixed with lead ores (if they are not already rich enough in lead), and the two metals are obtained as an alloy. The separation will be described on page 751.

2. **Hydrometallurgy.** In this process the silver is dissolved from the finely crushed ore by a solution of some suitable reagent. Sometimes sulfide ores are roasted until the silver is converted into sulfate, which is itself soluble in water. In other cases, solutions of sodium cyanide, sodium mercurous cyanide, $NaHg(CN)_2$, or sodium thiosulfate are employed, all of which dissolve silver, as well as some silver compounds. From the solution of silver so obtained the metal is precipitated by a suitable reagent, such as copper, zinc, or sodium sulfide. Copper or zinc precipitates it directly; sodium sulfide precipitates it as silver sulfide (Ag_2S), which is filtered off and heated with aluminum. This precipitates metallic silver. The precipitated silver is then refined.

Refining of Silver · There are a number of methods by which silver is refined, two of which may be mentioned:

1. **Cupellation and parting with sulfuric acid.** In this process the metal, alloyed with a large excess of lead, is heated on an open hearth in a strong current of air. The various metallic impurities (excepting gold) are in this way largely converted into oxides and swept off as *dross*, leaving the silver alloyed with small percentages of gold, copper, and iron. It is then cast into ingots known as *doré* bars, since they contain gold.

In order to recover the gold, the alloy is treated with hot concentrated sulfuric acid, which converts all the metals, except the gold, into sulfates. When water is added to the resulting mixture, the sulfates of copper, silver, and iron pass into solution, while the gold and other unattacked substances settle as a mud, from which the gold is subsequently recovered. The silver is separated from the solution of the sulfates by suspending in the latter clean copper plates, the copper displacing the silver, which is deposited in crystalline form:

$$Ag_2SO_4 + Cu \longrightarrow CuSO_4 + 2\,Ag\downarrow$$

The copper sulfate obtained as a by-product in this process furnishes much of the blue vitriol of commerce.

2. **Electrolytic refining.** Electrolysis of the impure silver is now carried out extensively, the process being conducted in a way very similar to the electrolysis of copper. The electrolyte used is a solution of silver nitrate in nitric acid. The silver is deposited as crystals, which are mechanically brushed off the cathode, collected, and melted into bars.

Chemical Properties · Silver is one of the inactive elements. It does not combine directly with oxygen, hydrogen, carbon, nitrogen, or silicon, nor is it acted upon by dilute acids or fused alkalies. The halogen elements attack it slowly and only superficially, since impervious halides are formed which prevent further action. Ozone attacks it, forming a black peroxide. Sulfur, as well as most sulfur compounds, blackens it, owing to the formation of silver sulfide ("oxidized silver"). The strong oxidizing acids dissolve it, forming the corresponding salts, such as the nitrate, $AgNO_3$, and the sulfate, Ag_2SO_4. Sodium cyanide, in the presence of air and water, dissolves it according to the following equation:

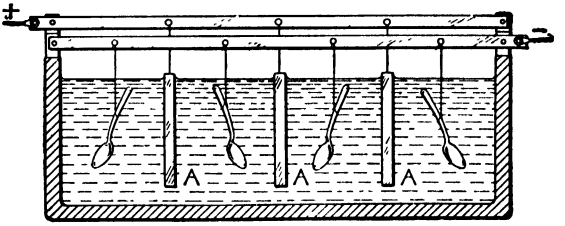


Fig. 41-2. Silver Plating · The article to be plated is made the cathode, plates of silver (*A*) the anode, and a soluble silver salt the electrolyte

$$8\,NaCN + O_2 + 2\,H_2O + 4\,Ag \longrightarrow 4\,NaAg(CN)_2 + 4\,NaOH$$

Since silver has a pleasing appearance and is not acted upon by water or air, it is used to electroplate various articles made of cheaper metals (Fig. 41-2, p. 713).

Compounds of Silver · Silver in its oxidation state of + 1 forms a well-defined series of salts. These salts are usually colorless or light yellow. Most of them are barely soluble in water and are little hydrolyzed. They are readily reduced to metallic silver, and consequently are mild oxidizing agents. The salts of silver are characterized by the fact that very few of them form hydrates. Silver exists also in oxidation states of + 2 and + 3, but the compounds formed in these states are unstable.

Silver Oxide (Ag_2O) · Silver oxide is formed as a dark-brown amorphous precipitate when a soluble hydroxide is added to a solution of a silver salt, the hydroxide at first formed spontaneously decomposing into water and the oxide. It is sufficiently soluble in water to turn red litmus blue, evidently forming some hydroxide, which acts as a strong, highly ionized base. It reacts with strong acids to form salts which are neutral to indicators. At a very moderate temperature it decomposes into silver and oxygen, the reaction being rapid at 250°. The common antiseptics known as Protargol and Argyrol consist of colloidal compounds of silver oxide and protein derivatives.

Silver Halides · Silver fluoride (AgF) is prepared by dissolving silver oxide in hydrofluoric acid. It is a very soluble salt, crystallizing as the hydrates $AgF \cdot H_2O$ or $AgF \cdot 2\,H_2O$. The other halides, on the contrary, are practically insoluble, the chloride being the most soluble of the three and the iodide the least so. They are prepared by treating a soluble silver salt with either a soluble halide salt or the free acid:

$$AgNO_3 + HCl \longrightarrow AgCl\downarrow + HNO_3$$

They form amorphous, curdy precipitates, the chloride being white, the bromide very pale yellow, the iodide decidedly yellow. All three are also known in crystalline condition. The formation of these precipitates is used as a test, on the one hand for silver ions and on the other for the halogen ions. The halides are soluble in a number of normal salts, forming a series of complex compounds. This property is of importance in metallurgy and in photography. The chloride is soluble also in ammonium hydroxide, forming the ammino salt $Ag(NH_3)_2Cl$, which can be obtained in the form of shining, colorless needles. When treated with gaseous ammonia, silver halides form ammoniates, such as $2\,AgCl \cdot 3\,NH_3$ and $AgCl \cdot 3\,NH_3$.

All three of the insoluble silver halides are sensitive to light. When exposed to bright light, they soon darken in color as the result of a change

in which a portion of the halogen element is liberated. It is upon this property of these halides that the art of photography is based.

Silver Nitrate (Lunar Caustic) ($AgNO_3$) · Silver nitrate is prepared by the action of nitric acid upon silver, and it is the salt of silver most extensively used in the laboratory. It is extremely soluble in water, 100 g of solvent at 20° dissolving 215 g, and at 100°, 910 g. It crystallizes in colorless rhombic plates and melts undecomposed at 212°. It is often cast into sticks for use as a caustic in surgery, its use depending upon the fact that it is a powerful oxidizing agent. It produces a black stain on the skin, owing to a deposit of metallic silver. A similar stain is produced upon any other oxidizable material, such as cloth, and because of this fact silver nitrate is used in the manufacture of indelible inks. It dissolves in aqua ammonia, forming the ammino salt $Ag(NH_3)_2NO_3$.

Other Silver Salts · Among important soluble salts are the following:

Silver sulfate (Ag_2SO_4), sparingly soluble in water.
Silver acetate ($AgC_2H_3O_2$), crystallizing in shining needles.
Silver nitrite ($AgNO_2$), slightly soluble in water.

Some insoluble salts important in chemical analysis are these:

Silver sulfide (Ag_2S), found in nature as *argentite*. As prepared by precipitation, it is a black amorphous solid. It is the most insoluble of silver compounds.

Silver cyanide (AgCN), a curdy white precipitate formed when a soluble cyanide is added to a silver salt. It is soluble in excess of the precipitant, forming a complex cyanide:

$$AgCN + KCN \longrightarrow KAg(CN)_2$$

Silver carbonate (Ag_2CO_3), a pale-yellow powder.
Silver chromate (Ag_2CrO_4), a brick-red amorphous solid.
Silver phosphate (Ag_3PO_4), a clear yellow solid.
Silver pyrophosphate ($Ag_4P_2O_7$), a granular white powder.

Photography

Silver and Photography · Next in importance to the use of silver for coinage comes its use for sterling silver and then for photography (Fig. 41-3). Photographic plates and films annually absorb more than 6,000,000 oz of silver, and much of this is permanently lost. The "movie" films made in an average year, if placed end to end, would encircle the earth several dozen times.

The process of photography in its simplest form may be described briefly as follows:

1. **Preparation of the negative.** The negative is made by spreading a thin layer of gelatin, in which colloidal silver bomide is suspended (silver iodide is sometimes added also), over a film of cellulose acetate (or over a glass plate) and allowing it to dry. When the film so prepared is placed in a camera and the image of some object is focused upon it, the silver salt undergoes a decomposition, the amount of which is proportional at every point to the intensity of the light falling upon it and to the time of exposure. In this way an image of the object photographed is produced upon the film. This image, however, is invisible and is therefore called *latent*. It can be made visible by the process of *developing*.

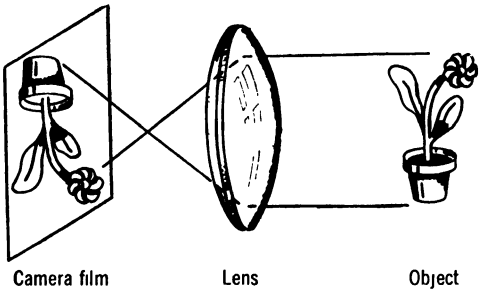


Fig. 41-3. Diagram Showing a Camera Film upon Which the Image of an Object Is Focused by a Lens

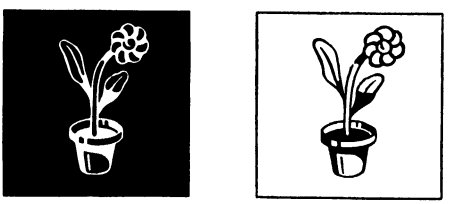
To develop the image the exposed film is immersed in a solution of some reducing agent, called the *developer*. While the developer will *in time* reduce all the silver salt, it acts much more rapidly upon that which has been exposed to the light. The action is therefore continued only long enough to bring out the image. The reduced silver is left in the form of a black deposit.

The unchanged silver salt is now removed from the film by dipping it in a solution of sodium thiosulfate (*hypo*, p. 293). The sodium thiosulfate and silver halide react to form a *soluble* complex salt, sodium silver thiosulfate:

$$AgBr + 2\ Na_2S_2O_3 \longrightarrow Na_3Ag(S_2O_3)_2 + NaBr$$

The film is then washed with water and dried. The film so prepared is called the *negative* (Fig. 41-4) because it is a picture with the lights and darks exactly reversed.

2. **Preparation of the print.** The print is made on paper coated with gelatin and silver halide in much the same way as the negative. The negative is placed on the paper and exposed to the light in such a way that the light must pass through the negative before striking the paper. If the paper is coated with silver chloride, a visible image is produced and a developer may not be needed; proofs are made in this way. The image gradually darkens on further exposure to light unless the unchanged silver chloride is dissolved off with sodium thiosulfate. Many papers are coated with silver bromide, or with mixtures of silver bromide and silver chloride, and must then be developed and treated with hypo, exactly as required in finishing the negative. If desired, the print may be *toned* by dip-



Negative, with original lights and darks reversed

Positive, with original lights and darks restored

Fig. 41-4. Difference between the Negative and a Print

ping it into a solution of salts of gold or of platinum, in which process the silver on the print passes into solution, gold or platinum replacing it. Since the darkest places on the negative cut off the most light, the lights of the print (Fig. 41-4) will be the reverse of those of the negative and will correspond to those of the object.

The light-sensitive silver halides are most affected by violet and ultraviolet light waves. Reagents have been found that are sensitive to the longer red waves. The longer waves are not so easily absorbed by water vapor in the air, and with them photographs can be taken even through clouds.

Gold

Occurrence · From the earliest times gold has been known as a precious metal. It was called *aurum* by the Romans, and from this name the symbol Au is derived. For the most part it is found as metallic gold, either embedded in quartz veins or as grains or large nuggets in the heavy sands resulting from the weathering of quartz rock. Usually the native gold contains small quantities of other metals, such as silver, copper, and lead. In compound form it occurs in a number of minerals, nearly all of which contain tellurium together with silver and copper. A little gold telluride is apparently dissolved in the sulfides of many other metals, such as those of copper, lead, and silver; and gold is obtained as a by-product in the refining of these metals. South Africa produces approximately one half of the world's output of gold; Canada produces about 11 per cent and the United States considerably less. The production in the United States and its possessions dropped from nearly 6,000,000 troy ounces in 1941 to about 930,000 in 1945, because of wartime regulations, and recently has come up to about 38,000,000 ounces, with Utah, California, Colorado, Nevada, Arizona, and Alaska as the leading producers.

Physical Properties · Gold is a yellow metal which melts at about the same temperature as copper and boils at approximately 2500°. It is about as soft as silver, is a good conductor of electricity, and is the most ductile and malleable of the metals. It forms alloys with most metals, and its uses are too familiar to require description. In a pure condition gold is too soft to be used for jewelry and coinage, and for such purposes it is always alloyed with copper or silver or both. The fineness of gold is usually expressed in terms of carats, 24-carat gold being pure, while 18-carat (75 per cent) is the grade used for the best jewelry. For coinage a 90 per cent alloy is used. It has been estimated that if all the monetary gold in the world were to be cast into one large cube, the cube would

have an edge length of somewhat more than 30 ft and would weigh in the neighborhood of 20,000 tons.

Mining and Extraction · Native gold is recovered in crude form by *placer* mining. The sand containing the gold is shaken or stirred in troughs of running water, called *sluices*. This sweeps away the sand but allows the heavier gold to sink to the bottom of the sluice. Sometimes the sand containing the gold is washed away from its natural location into the sluices by powerful jets of water. This is called *hydraulic* mining. In *vein* mining the gold-bearing quartz is stamped into fine powder in stamping mills, and the gold is extracted by a number of processes, two of which are the following:

1. **Amalgamation process.** In the amalgamation process the powder containing the gold is washed over a series of copper plates whose surfaces have been coated with mercury. The gold sticks to the mercury or alloys with it (see page 727), and after a time the gold and mercury are scraped off and the mixture is distilled. The mercury distills off, and the gold is left in the retort, ready for refining.

2. **Cyanide process.** This process depends upon the fact that gold is soluble in a solution of sodium cyanide in the presence of the oxygen of the air. The powder from the stamping mills is treated with a very dilute sodium cyanide solution, which dissolves the gold:

$$4\ Au + 8\ NaCN + 2\ H_2O + O_2 \longrightarrow 4\ NaOH + 4\ NaAu(CN)_2$$

From this solution the gold can be obtained by electrolysis or by precipitation with metallic zinc:

$$2\ NaAu(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2\ Au\downarrow$$

Refining of Gold · Gold is refined by four general methods:

1. **Electrolysis.** When gold is dissolved in a solution of sodium cyanide and the solution electrolyzed, the gold is deposited in very pure condition on the cathode.

2. **Cupellation.** When the gold is alloyed with easily oxidable metals, such as copper or lead, it may be refined by cupellation. The alloy is fused with an oxidizing flame on a shallow hearth made of bone ash, which substance has the property of absorbing metallic oxides but not the gold. Any silver which may be present remains alloyed with the gold.

3. **Parting with sulfuric acid.** Gold may be separated from silver, as well as from many other metals, by heating the alloy with concentrated sulfuric acid. This dissolves the silver, while the gold is not attacked. Sometimes nitric acid is used instead of sulfuric acid.

4. **Action of chlorine on molten alloy.** The crude alloy is melted, and chlorine gas is bubbled through it. The silver and copper are converted into chlorides (solids) and are skimmed off. The residual gold is then put into solution and separated by electrolysis.

Chemical Properties · Gold is not attacked by any one of the common acids. It is easily dissolved by solutions containing free chlorine or bromine, by aqua regia, and by solutions of sodium cyanide in the presence of air. Fused alkalies also corrode the metal, with the formation of aurates of the general type $KAuO_2$.

In its compounds gold nearly always acts as a trivalent element. Auric hydroxide, $Au(OH)_3$, yields two series of compounds. One is represented by such salts as the chloride, $AuCl_3$, while the other consists of aurates, such as potassium aurate ($KAuO_2$).

Complex Compounds · The great majority of the compounds of gold are complex compounds, such as cyanides and ammonia derivatives. Among the most important is *chloroauric acid* ($HAuCl_4$), formed by dissolving gold in aqua regia. The sodium salt ($NaAuCl_4 \cdot 2\ H_2O$) is used as a toning reagent in photography. The cyanides $KAu(CN)_2$ and $KAu(CN)_4$ are used as electrolytes in gold-plating. One of the most characteristic reactions of gold compounds is the production of a purple precipitate known as the *purple of Cassius*, when a solution containing stannous chloride and stannic acid is warmed with a very dilute solution of a gold salt. The gold salt is reduced by the stannous chloride, and purple colloidal gold is precipitated along with colloidal stannic acid.

QUESTIONS

1. What metals have a distinguishable color?

2. What elements are liquid at ordinary temperatures?

3. Copper, silver, and gold are sometimes called the currency metals. Why?

4. Is it safe practice to use copper pipes for conveying drinking water? Explain.

5. Which cell will furnish the higher voltage, (*a*) one having electrodes of zinc and copper or (*b*) one having electrodes of zinc and silver? Explain.

6. All cuprous salts have a marked tendency to undergo a spontaneous oxidation-reduction reaction according to the equation $2\ Cu^+ \longrightarrow Cu^{++} + Cu$. Why, then, is it possible to prepare cuprous chloride by the reaction of metallic copper on cupric chloride?

7. Why not prepare silver chloride like mercurous chloride, that is, by heating silver sulfate with salt?

8. Silver oxide is easily prepared. Why is it not formed, together with lead oxide, in the cupellation process?

9. In parting silver from gold with sulfuric acid, silver is converted into silver sulfate. Write the equation.

10. Why does the addition of sodium carbonate to a solution containing compounds of copper sometimes cause a precipitate and sometimes not?

11. The following reactions can be carried out consecutively in the same beaker. (All insoluble compounds are indicated by $\downarrow$, and all reagents are written over the horizontal arrow.)

$$AgNO_3 \text{ (solution)} \xrightarrow{NaOH} Ag_2O\downarrow \xrightarrow{NaCl} AgCl\downarrow \xrightarrow{NH_4OH} Ag(NH_3)_2^+ \xrightarrow{NaBr} AgBr\downarrow$$
$$\xrightarrow{Na_2S_2O_3} Ag(S_2O_3)_2^{---} \xrightarrow{NaI} AgI\downarrow \xrightarrow{NaCN} Ag(CN)_2^- \xrightarrow{H_2S} Ag_2S\downarrow$$

a. List the insoluble substances in the order of their solubilities.

b. Write the solubility-product formula for each of the insolubles and explain by it why each of these (except Ag_2S) dissolves in the reagent indicated.

c. From this information would you predict that silver chloride is soluble in potassium cyanide solution? silver bromide in ammonium hydroxide solution?

d. Write equations for all the reactions involved.

12. What analytical test can be used to distinguish between Cu^{++} and Ag^+ ions?

PROBLEMS

1. What weight of chalcopyrite will be required to furnish the copper for 100 kg of silver dollars?

2. What weight of 98 per cent sulfuric acid will be required to part the silver from the gold in 100 g of an alloy containing 80 per cent silver?

3. One gram of a silver dollar was dissolved in nitric acid, and the silver was precipitated as silver chloride. The precipitate weighed 1.1957 g. Was the dollar genuine?

4. A number of old "movie" films were soaked in sodium thiosulfate, and the solution was diluted to 1 liter. Five cubic centimeters of the solution was decomposed by hydrochloric acid, and the silver was collected and weighed as silver chloride. It weighed 2 g. How much silver could be recovered from the remainder of the solution?

CHAPTER 42

ZINC, CADMIUM, AND MERCURY

General · Zinc, cadmium, and mercury form the first family following the transition elements. Their atoms have two valence electrons overlying a completed shell of eighteen. The elements, therefore, resemble the

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	BOILING POINT	ELECTRONS IN SHELLS
Zinc (Zn)	65.38	30	7.14	419.4	907°	2, 8, 18, 2
Cadmium (Cd) .	112.41	48	8.65	320.9	767°	2, 8, 18, 18, 2
Mercury (Hg) . .	200.61	80	13.55	− 38.87	357°	2, 8, 18, 32, 18, 2

alkaline-earth elements in many of their chemical properties. They differ from the alkaline-earth metals in having a much higher density and in the fact that their hydroxides are considerably less basic.

Zinc, cadmium, and mercury exhibit a maximum oxidation state of + 2. They are much less electropositive than the alkaline-earth elements, resembling the transition elements when the latter show their valence of + 2. They form halides which are only slightly dissociated in solution. Mercury is below hydrogen in the electrochemical series; hence it requires a stronger oxidizing agent than hydrogen ions to oxidize it. Zinc and cadmium have many properties in common, but most of the compounds of mercury differ considerably from those of zinc and cadmium; it is often said that mercury is the most unpredictable element known with regard to the kinds and properties of the compounds which it forms.

Zinc and Its Compounds

Zinc is easily obtained from its ores, and possesses properties that make it useful for many purposes. As a result, it has long been known and used. Jewelry made of zinc has been found in the ruins of cities that were destroyed before the beginning of the Christian Era.

Occurrence and Metallurgy · Zinc does not occur free in nature. It is not a constituent of common rocks, and its occurrence is rather local and confined to deposits or pockets. Its chief ores are *sphalerite* (ZnS); *zincite* (ZnO); *smithsonite* ($ZnCO_3$); *willemite* (Zn_2SiO_4); *calamine* ($Zn_2SiO_4 \cdot H_2O$); *franklinite* ($ZnFe_2O_4$). In the United States it occurs

in a number of different localities, but most abundantly in New Jersey and in the so-called "Tri-State District," made up of different parts of Oklahoma, Missouri, and Kansas. The United States produces about 900,000 tons, annually.

In the metallurgy of zinc the ores are first converted into the oxide by roasting, and the oxide is then reduced with carbon.

A mixture of zinc oxide and coal is heated in earthenware retorts. The zinc oxide is thereby reduced, and the resulting zinc, being volatile at the temperature of the retort, distills and is collected in suitable receivers. At first the zinc collects in the form of a powder known as *zinc dust* (*blue powder*), which, however, contains about 5 per cent of zinc oxide. Later, when the receiver has become hot, the zinc condenses to a liquid and is drawn off into molds. In this form it is impure and is known as *spelter*.

Large quantities of zinc are now produced by the electrolysis of zinc sulfate. The ore is first dissolved in sulfuric acid, and the cadmium, silver, and copper present are removed by the addition of metallic zinc.

Commercial zinc usually contains a number of impurities, especially carbon, arsenic, cadmium, and iron. These can be largely removed by redistillation. Zinc containing less than 0.001 per cent of impurities has been obtained by the electrolysis of a pure salt and subsequent distillation under diminished pressure.

Properties · Pure zinc is a bluish-white metal. Some of its physical properties are greatly modified by the temperature and the previous treatment of the metal. When allowed to solidify from the liquid state, it is highly crystalline and is quite hard and brittle. At temperatures between 100° and 150° it is malleable and can be rolled into thin sheets, which retain their softness and malleability at ordinary temperatures. Above 150° it again becomes very brittle. When melted and poured slowly into water, it forms thin, brittle flakes, and in this condition is called *granulated zinc* or *mossy zinc*.

Zinc tarnishes superficially in moist air, owing to the formation of a basic carbonate. It does not decompose even boiling water, but at a high temperature it acts upon steam, forming the oxide and hydrogen. When heated sufficiently in oxygen or air, it burns with a bluish-white flame. Dilute acids act very slowly upon the pure metal, since the hydrogen at first liberated collects on the surface in the form of a thin protecting film. If another metal below zinc in the electrochemical series, such as iron, copper, or platinum, is present, either as an impurity or simply in contact with the zinc, the hydrogen escapes from the surface of the more positive metal, and the zinc rapidly dissolves. Zinc also dis-

solves in solutions of the hydroxide of sodium or potassium, with liberation of hydrogen, the equation probably being

$$Zn + 2\,OH^- + 2\,H_2O \longrightarrow Zn(OH)_4^{--} + H_2\uparrow$$

Uses of Zinc · The chief use of the metal is to protect the surface of iron against rust. *Galvanized iron* is made either (1) by dipping sheets of iron into melted zinc, (2) by electroplating, or (3) by blowing melted zinc on the iron with a spray gun. *Sherardized iron* is prepared by heating the iron in contact with a mixture of zinc dust and zinc oxide in closed vessels. About two thirds of all the zinc produced is used in these ways. Large quantities are used in the manufacture of alloys, particularly brass (see the table of alloys on page 708). The metal is also used in the construction of batteries, as a roofing material, and in the metallurgy of silver and gold. In the laboratory it is used in the preparation of hydrogen and as a reducing agent.

Compounds of Zinc · In general, the compounds of zinc are similar in formula and appearance to those of magnesium. They often differ from them markedly, however, in chemical properties. Either the metal, its oxide, or the natural carbonate or sulfide serves as a convenient material for the preparation of these compounds.

Zinc Oxide (Zinc White) (ZnO) · This is a white powder obtained by burning mixtures of the oxidized zinc ores and coal in a forced draft, and collecting the resulting fumes of zinc oxide. It is used very largely as a white pigment in paints, under the name of *zinc white*, and has an advantage over white lead in that it is not darkened by the sulfur compounds which are present in the air, especially in manufacturing districts. Zinc oxide is used as a filler in the manufacture of rubber goods, chiefly automobile tires and as a component of glazes, enamels, and glass.

Zinc Hydroxide ($Zn(OH)_2$) · This compound is precipitated in the form of a white solid when an alkali is added to a solution of a zinc salt. It is an amphoteric hydroxide, dissolving in both acids and alkalies.

$$Zn(OH)_2 + 2\,H^+ \longrightarrow Zn^{++} + 2\,H_2O$$

Soluble Salts · The soluble salts of zinc can be prepared by dissolving the metal or its oxide in the appropriate acid. The chloride and sulfate are the most familiar.

Zinc Chloride ($ZnCl_2$) · This salt is readily soluble in water and in alcohol. It is strongly hydrolyzed in water, and upon evaporation the solution yields a basic chloride, ZnOHCl, in addition to zinc chloride. The largest use of zinc chloride is as a wood preservative, since it kills the bacteria that cause decay.

Zinc Sulfate ($ZnSO_4$) · Under ordinary conditions this salt crystallizes from water in the form of a heptahydrate, $ZnSO_4 \cdot 7\ H_2O$, which has long been known under the name of *white vitriol.* Commercially the salt is prepared by roasting sphalerite, leaching the resulting zinc sulfate, and purifying it by crystallization. It is used in medicine, and to a limited extent in the dyeing and printing of cloth.

Insoluble Salts · These are prepared by the ordinary methods of precipitation. The most important ones are the sulfide and carbonate. The normal carbonate, $ZnCO_3$, is precipitated when sodium bicarbonate is added to a solution of a zinc salt. Normal sodium carbonate precipitates basic salts, as in the case of magnesium.

Zinc Sulfide (ZnS) · The natural zinc sulfide (sphalerite, blende, or blackjack) varies, largely according to the impurities present, from a light-yellow, transparent, resinous solid to a black mass. As prepared in the laboratory by precipitation, it is a white solid. The fact that zinc is the only one of the common metals that forms a *white* insoluble sulfide is of importance in chemical analysis.

Formation of Zinc Sulfide by Precipitation · Zinc sulfide is nearly insoluble in water and is formed as a precipitate when ammonium sulfide is added to a solution of a salt of zinc:

$$ZnCl_2 + (NH_4)_2S \longrightarrow ZnS\downarrow + 2\ NH_4Cl \qquad (1)$$

On the other hand, when hydrogen sulfide is passed into such a solution, the precipitation of the zinc sulfide soon ceases, an equilibrium resulting, as expressed in the equation

$$ZnCl_2 + H_2S \rightleftarrows ZnS\downarrow + 2\ HCl \qquad (2)$$

because the H^+ ions produced reach a high enough concentration to reverse the reaction at an appreciable rate (p. 434). If the H^+ ions are buffered with a salt such as sodium acetate, this reaction can be driven to completion.

In accordance with the theory of precipitation (p. 460) this equilibrium results in the following way: While zinc sulfide is commonly said to be insoluble, because it is nearly so, it really has a very perceptible solubility. Before it can begin to precipitate, the concentration of the zinc ions and sulfide ions must be large enough to exceed the solubility product (K_{sp}) of the zinc sulfide:

$$[Zn^{++}] \times [S^{--}] > K_{sp} \qquad (3)$$

An abundant concentration of the zinc ions is supplied by the zinc salt; moreover, at the beginning of the reaction the concentration of the sulfide ions derived from the hydrogen sulfide,

$$H_2S \rightleftarrows H^+ + HS^- \qquad (4)$$
$$HS^- \rightleftarrows H^+ + S^{--} \qquad (5)$$

is large enough so that the solubility product of the zinc sulfide is exceeded, and

precipitation takes place. As the reaction proceeds, however, the removal of sulfide ions causes the ionization equilibria for the hydrogen sulfide (equations (4) and (5)) to shift toward the right, and the hydrogen ion concentration increases as a result.

In the presence of hydrogen ions the concentration of sulfide ions in equilibrium with the hydrogen sulfide is smaller than in a neutral solution. As the hydrogen ion concentration increases, the fraction of the hydrogen sulfide existing as sulfide ions becomes so small that a very high concentration of zinc ions is necessary to exceed the value of the solubility product of the zinc sulfide; hence the precipitation ceases when the concentration of the zinc ions in solution is still appreciable. However, if a normal *salt of some weak acid*, such as sodium acetate ($NaC_2H_3O_2$), is added to the solution of the zinc salt, and the hydrogen sulfide then passed in, the precipitation of the zinc sulfide continues to completion; for as fast as the hydrogen ions are formed in the reaction, they enter into an equilibrium with the anion of the weak acid, as shown in the following equation:

$$H^+ + C_2H_3O_2^- \rightleftarrows HC_2H_3O_2$$

This keeps the concentration of the hydrogen ions too low to have any marked effect upon the concentration of the sulfur ions, so that precipitation continues to completion. It may be stated that the addition of sodium acetate to an acid solution is a device often employed when it is desired to reduce the concentration of the hydrogen ions to a minimum value and yet have the solution distinctly acid in reaction. This mixture of salt and acid is called a *buffer solution* (p. 456).

Cadmium and Its Compounds

Until recently the chemistry of cadmium has been mainly of academic interest; but with the several present industrial uses of cadmium, its chemistry is becoming of greater practical interest.

Occurrence and Preparation · Cadmium is associated with zinc ores in nature, small quantities occurring in many zinc ores in about the ratio of 1 part of cadmium to 200 parts of zinc. In the course of the metallurgy of zinc the cadmium compounds are changed to cadmium oxide, which is then reduced by carbon, the cadmium distilling over with the zinc. Being more volatile than the zinc, it is largely concentrated in the first portions of the distillate. From these portions the pure metal can be obtained by fractional distillation. The metal resembles zinc in appearance and properties.

Production and Uses · The normal annual production of cadmium in the United States amounts to about 10,000,000 lb. Until recent years there were few important uses for the metal. It was a component in a number of low-melting alloys used for electric fuses, automatic fire-

extinguishers, safety plugs in steam boilers, bearing metals, and dental alloys. It was alloyed with silver to prevent easy tarnishing, and with gold to make it green in color. It had great scientific value as the cathode metal in the electric cell used as a standard of voltage.

It was necessary to separate cadmium from the zinc that was to be made into zinc white, for cadmium oxide is dark-brown. Consequently there was an oversupply. Now it has been found that cadmium is better than zinc for protecting iron and other metals from rust and tarnish, and it is coming into wide use. It can be applied in the melted state as a spray or by electroplating. It takes a good polish and also affords a good base for further plating with other metals. It is especially well adapted to covering gasoline tanks and small automobile parts.

Compounds of Cadmium · Some of the most important of the compounds of cadmium are the following: *Cadmium oxide* (CdO) is obtained by heating cadmium in air or oxygen. It is a brown powder and combines with water to form *cadmium hydroxide* ($Cd(OH)_2$), a white insoluble solid. *Cadmium chloride* ($CdCl_2$) crystallizes from water as the dihydrate. *Cadmium bromide* ($CdBr_2$) and *cadmium iodide* (CdI_2) resemble the chloride and are used to some extent in photography. *Cadmium sulfate* crystallizes from water as a hydrate of the formula $(CdSO_4)_3 \cdot 8\ H_2O$, while under similar conditions *cadmium nitrate* forms the hydrate, $Cd(NO_3)_2 \cdot 4\ H_2O$. *Cadmium sulfide* (CdS) is commercially the most important of the cadmium compounds. It occurs in nature in the form of the mineral known as *greenockite*. In the laboratory it is prepared by passing hydrogen sulfide into a solution of a cadmium salt. It is bright yellow in color and is used as a pigment and in making colored glass. Like zinc and copper, cadmium forms *complex ions* with ammonia—for example, $Cd(NH_3)_4^{++}$.

Mercury and Its Compounds

History and Occurrence · The element mercury, or *quicksilver*, as it is often called, was known considerably before the Christian Era and played an important part in the alchemy of the Middle Ages. It is found in a number of localities, usually in the form of a red sulfide called *cinnabar*, occasionally associated with drops of native metal. As a rule, the ores are not very rich, in many cases carrying less than 1 per cent of mercury. They can be concentrated by flotation. At present Italy produces the most mercury, followed by Spain, California, and Texas. It comes on the market in iron flasks, each flask containing about 75 lb. The annual production amounts to about 24,000 tons, of which the United States produces about 9 per cent.

Metallurgy · The metallurgy of mercury is extremely simple, owing to the ready decomposition of its compounds and the volatility of the metal. It is necessary only to roast the sulfide in a current of air:

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

The resulting vapor of mercury is easily condensed to a liquid.

Purification of Mercury · Solid materials that form a scum on the surface of mercury can be removed by filtration through soft leather. Dissolved metals (apart from gold) are first oxidized to water-soluble compounds by flowing the mercury in a fine stream through a dilute solution of ferric chloride or nitric acid contained in a tall vertical tube.

More perfect purification is attained by slow distillation in a partial vacuum, with a very small stream of oxygen drawn through the apparatus during distillation, as shown in Fig. 42-1.

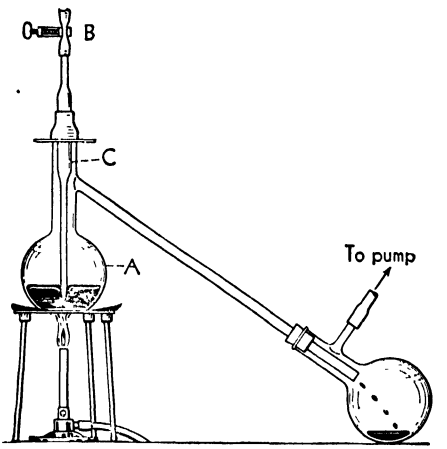


Fig. 42-1. Purification of Mercury Mercury is purified by distillation from the flask, *A*. The apparatus is partially evacuated by the pump, while a very small current of air is admitted at *B* and through the tube *C* (method of Hulett)

Properties and Uses of Metallic Mercury · Pure mercury is a silvery liquid at ordinary temperatures, and to this fact it owes the name *quicksilver* (the word *quick* meaning "live," or "moving"). It is a moderately good conductor of the electric current. Its various properties give it great value for scientific purposes, as in collecting gases that are soluble in water, constructing thermometers and barometers, making electrical contacts where rigid wires are troublesome, and many similar applications. It forms alloys (called *amalgams*) with nearly all metals, and the readiness with which it dissolves gold and silver has at times led to its extensive use in obtaining these metals from their ores.

The relatively high boiling point of mercury, 356.9°, has led to its use in high-temperature boilers, instead of water, and in vapor engines. The advantage of using a high-boiling liquid like mercury for such a purpose is that vapor engines, like steam engines, operate more efficiently, converting more of the available heat energy into mechanical energy, the higher the temperature of the vapor; and a high temperature can be achieved more easily with a liquid of high boiling point without, at the same time, producing a vapor pressure so high that the boiler might burst.

Fluorescent Lamps · When cold, mercury vapor does not conduct the electric current; but an arc is easily started in a vacuum tube containing the heated vapor, and a peculiar light, rich in green and ultraviolet rays, fills the tube. Such a tube, known as the Cooper-Hewitt lamp, has long been used. Its soft light is well adapted to night work in drafting rooms and factories. With tubes made of silica the transmitted light (ultraviolet) has good antiseptic properties and is used to destroy air-borne bacteria. If, in a mercury-vapor lamp, one electrode is iron and the other mercury, the vapor will conduct the current in one direction only, and such a lamp may be used as an electric-current rectifier.

The mercury-vapor lamps are greatly improved in the quality of the light emitted, and operate at a far less cost, when the inside of the tube is coated with compounds such as calcium or magnesium tungstate, zinc or cadmium silicate, zinc beryllium silicate, and cadmium borate, which fluoresce when the lamp is operated. A few milligrams of mercury is put into the coated tube, which is then evacuated. A little argon is admitted into the tube, which is thereupon sealed. At the beginning of use the argon carries the current while the mercury is being vaporized. The mercury vapors produce ultraviolet light, which excites fluorescence in the bodies coating the inside of the tube. These lamps have come into wide use.

Chemical Properties · Mercury is a metal of rather feeble chemical activity. It stands low in the electrochemical series, and is reduced to the free element by most of the common metals. When heated in the air at temperatures below its boiling point, it slowly combines with oxygen to form mercuric oxide, but this action is easily reversed at higher temperatures:

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

It does not displace hydrogen from acids; but ions that are stronger oxidizing agents than H^+ attack it, forming the corresponding salts. It has a greater tendency to combine with sulfur and the halogen elements than with oxygen.

Compounds of Mercury · Like copper, mercury forms *two* series of compounds, the mercurous and the mercuric. In general stability the two series are much more nearly equal than is the case with copper salts. Mercuric ions are reduced by mercury to form mercurous ions according to the reaction

$$Hg^{++} + Hg \longrightarrow Hg_2^{++}$$

For this reaction the equilibrium constant,

$$K = \frac{[Hg_2^{++}]}{[Hg^{++}]}$$

is equal to 81 at 18°. The reaction will be reversed if the mercuric compound is much less soluble than the mercurous compound; in other words,

under such conditions the mercurous compound will decompose (by autoxidation) to form Hg^{++} and Hg, and will maintain the value of the equilibrium constant. The validity of this prediction will be observed in the chemistry of mercurous oxide and sulfide.

Salts of the oxygen acids, as well as of practically all other acids, are known in each series. The salts of mercury are remarkable for the fact that, compared with other salts, they are very little ionized in solution. Also, the salts of mercury are much more generally soluble in organic solvents, such as alcohol and ether, than is usually the case with metallic salts. Both the metal and its salts are very poisonous. Nearly all compounds of mercury dissociate at high temperatures, yielding free mercury.

The mercurous ion is a double ion, as the formula Hg_2^{++} indicates. The reason for this association is not clearly understood. It is doubtful if the mercurous ion ever exists as Hg^{+}.

Mercurous Salts · Mercurous salts are obtained in either of two general ways.

1. **By precipitation.** The insoluble salts can be obtained by double decomposition with soluble mercurous salts, such as the nitrate, $Hg_2(NO_3)_2$:

$$Hg_2(NO_3)_2 + 2\ NaBr \longrightarrow Hg_2Br_2\downarrow + 2\ NaNO_3$$

2. **By reduction of a mercuric salt.** This is conveniently effected by the use of mercury as a reducing agent. Thus, mercuric chloride, when heated with mercury, yields mercurous chloride:

$$HgCl_2 + Hg \longrightarrow Hg_2Cl_2; \quad \text{or} \quad Hg^{++} + Hg \longrightarrow Hg_2^{++}$$

When mercury is dissolved in cold dilute oxidizing acids, the mercurous salt is obtained if mercury is in excess, for any mercuric salt which may be formed is then reduced.

Mercurous Oxide (Hg₂O) and Sulfide (Hg₂S) · These insoluble compounds are apparently formed by the usual methods of preparation, but they are very unstable and quickly decompose into the more stable mercuric compounds, especially under the influence of sunlight. The preparation and decomposition are illustrated in the equation for the sulfide:

$$Hg_2SO_4 + H_2S \longrightarrow H_2SO_4 + Hg_2S$$
$$Hg_2S \longrightarrow HgS\downarrow + Hg\downarrow$$

Mercurous Halides · The mercurous halogen compounds are comparatively stable and well characterized, the iodide being the least so. They are insoluble in water. The chloride, Hg_2Cl_2, known as *calomel*, is prepared by subliming mercuric chloride with mercury:

$$HgCl_2 + Hg \longrightarrow Hg_2Cl_2$$

It is also prepared by subliming mercurous sulfate with common salt. It is a white crystalline compound, easily volatilized, and has important uses as a drug. In strong sunlight the reaction just given is to some extent reversed, the preparation darkening in consequence of the separation of mercury. Since the mercuric chloride so formed is exceedingly poisonous, it is necessary to preserve calomel in dark bottles. The bromide, Hg_2Br_2, and the iodide, Hg_2I_2, have similar properties.

Mercurous Nitrate ***($Hg_2(NO_3)_2$)*** · This salt is formed when cold dilute nitric acid acts upon mercury. It is very soluble, forms monoclinic needles of the hydrate, $Hg_2(NO_3)_2 \cdot 2\,H_2O$, and undergoes hydrolysis in dilute solution, forming a basic salt.

Mercurous Sulfate ***(Hg_2SO_4)*** · Mercurous sulfate is formed in a similar way by the action of sulfuric acid upon mercury. It is used in making standard electric cells.

Mercuric Salts · Mercuric salts are usually prepared by the oxidation of mercurous salts, or by the solution of mercuric oxide or mercury in the appropriate acid. As a rule, they are more soluble than the corresponding mercurous salts and are more extensively hydrolyzed in solution, yielding a great variety of basic salts, which are usually of some shade of yellow. They yield also many complex compounds.

Mercuric Oxide ***(HgO)*** · Mercuric oxide is prepared as a bright-red crystalline powder by the careful heating of mercuric nitrate. It is obtained also as a yellow precipitate when a cold solution of a soluble base is poured into a solution of a mercuric salt. The hydroxide, which would be expected to form in the reaction, spontaneously decomposes into the oxide:

$$Hg(OH)_2 \longrightarrow HgO\downarrow + H_2O$$

The yellow oxide changes into the red at a higher temperature. When the oxide is heated, it dissociates into mercury and oxygen, a reaction which led Priestley to the discovery of oxygen.

Mercuric Chloride ***(Corrosive Sublimate)*** ***($HgCl_2$)*** · Mercuric chloride can be obtained by the usual methods as a white crystalline solid, moderately soluble in water. In the industries it is made by heating a mixture of ordinary salt and mercuric sulfate, and condensing the volatile chloride. It is soluble in alcohol and in ether, as well as in water, and is extensively used in surgery as an antiseptic. It is extremely poisonous. It combines directly with a great variety of substances, among others with albumin. This latter fact leads to the use of white of egg as an antidote for the compound, though no known antidote is very effective. When treated with a reducing agent, it is easily reduced to mercurous chloride and often

to free mercury. The reactions with stannous chloride, for example, are shown in the following equations:

$$2\ HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2\downarrow + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2\ Hg\downarrow + SnCl_4$$

Mercuric Iodide (HgI$_2$) · This salt is interesting as occurring in two very different forms. At ordinary temperatures the stable form is bright scarlet in color. Above 126.5° this changes to a modified form, which is yellow, melting at 223°. When cooled below 126.5°, it changes again into the red form. It is very sparingly soluble in water, but dissolves readily in solutions of potassium iodide, forming the complex compound K_2HgI_4. This solution, with the addition of potassium hydroxide, is known as *Nessler's reagent*, and is used in detecting the presence of small traces of ammonia, especially in drinking waters.

Mercuric Sulfide (Cinnabar) (HgS) · Mercuric sulfide occurs in nature as the red mineral *cinnabar*, and is the most important natural compound of mercury. The compound can be obtained by precipitation, as shown in the following equation:

$$Hg(NO_3)_2 + H_2S \longrightarrow HgS\downarrow + 2\ HNO_3$$

When so prepared, it is a black amorphous substance, very highly insoluble in water and in acids. When mercury and sulfur are intimately ground together (forming the black amorphous sulfide) and the product is warmed with a solution of potassium sulfide (in which mercuric sulfide is somewhat soluble), the bright-red variety known as *vermilion* is obtained. It is a valuable pigment.

Other Mercuric Salts · A few other mercuric salts should be mentioned very briefly.

Mercuric cyanide, $Hg(CN)_2$, is a white solid, easily decomposed by heat into mercury and cyanogen.

Mercuric nitrate, $Hg(NO_3)_2$, crystallizes from dilute nitric acid in the form of a hydrate of the composition $Hg(NO_3)_2 \cdot 8\ H_2O$. In water it undergoes hydrolysis, with the formation of basic salts.

Mercuric sulfate, $HgSO_4$, is known both as the anhydrous salt and as the monohydrate, $HgSO_4 \cdot H_2O$. Both salts are white crystalline solids, which hydrolyze, forming a yellow basic salt of the formula $HgSO_4 \cdot 2\ HgO$.

Mercuric fulminate, $Hg(ONC)_2$, is prepared by the action of nitric acid upon mercury in the presence of alcohol. It is extremely explosive and is used in the manufacture of primers for cartridges.

Ammonia Compounds of Mercury · Among the most numerous complex compounds of mercury are those which its salts form with ammonia. Many other metals form similar compounds, but those of mercury are among the best known. This class of compounds was extensively studied by the American chemist E. C. Franklin. They can be understood most

easily by remembering that liquid ammonia and water, as solvents, have many qualities in common, and that their reactions are closely analogous. The organic derivatives of ammonia have already been discussed (p. 533); the analogies in inorganic chemistry include the following:

1. **Analogues of hydrates.** Just as a salt may take up water to form a hydrate, so it may combine with ammonia to form an *ammonate*:

$$CuCl_2 + 2\ NH_3 \longrightarrow CuCl_2 \cdot 2\ NH_3$$
$$HgCl_2 + 2\ NH_3 \longrightarrow HgCl_2 \cdot 2\ NH_3$$

2. **Analogues of basic salts.** The hydrolysis of salts has already been explained (p. 457) and is well illustrated in the case of bismuth chloride, in which the following stages occur:

$$Bi\begin{matrix}Cl\\Cl\\Cl\end{matrix} \longrightarrow Bi\begin{matrix}OH\\Cl\\Cl\end{matrix} \longrightarrow Bi\begin{matrix}OH\\OH\\Cl\end{matrix} \longrightarrow Bi\begin{matrix}O\\\\Cl\end{matrix} + H_2O$$

With mercuric salts there is a corresponding action, which Franklin aptly named *ammonolysis*. With the chloride the stages are

$$Hg\begin{matrix}Cl + H\\Cl\end{matrix}NH_2 \longrightarrow Hg\begin{matrix}NH_2\\Cl\end{matrix} \longrightarrow Hg\begin{matrix}NH_2\\NH_2\end{matrix} \longrightarrow HgNH + NH_3$$

Compounds of this type, formed by ammonolysis and analogous to basic salts, are called *ammonobasic* salts.

3. **Mixed types.** When mercury salts are treated with *aqueous* ammonia, which may be regarded as a mixed solvent consisting of water and ammonia, *both hydrolysis and ammonolysis may occur.* In the case of the chloride this is represented by the equation

$$Hg\begin{matrix}Cl + H{-}OH\\Cl + H{-}NH_2\end{matrix} \longrightarrow Hg\begin{matrix}OH\\NH_2\end{matrix} + 2\ HCl$$

The product of this reaction is both *water-basic* and *ammonobasic.*

Reactions which can be referred to these types occur with most mercuric salts. With mercurous salts there is at the same time a decomposition which results in the formation of a mercuric derivative and free mercury, as is illustrated in the case of calomel:

$$2\ Hg_2Cl_2 + 4\ NH_3 + H_2O \longrightarrow Hg\begin{matrix}Cl\\NH_2\end{matrix} + Hg + Hg_2O + 3\ NH_4Cl$$

The ammonobasic mercuric chloride formed in this reaction is a white compound, but it appears to be jet-black, owing to the finely divided mercury precipitated at the same time.

QUESTIONS

1. How do you account for the differences in the properties of the zinc, cadmium, and mercury family and the calcium, strontium, and barium family?

2. Complete the following equations *if possible*; in case there is no reaction, indicate that fact:

a. $Zn + HCl \longrightarrow$
b. $Zn + H_2SO_4$ (dil.) $\longrightarrow$
c. $Zn + H_2SO_4$ (conc.) $\longrightarrow$
d. $Cd + HCl \longrightarrow$
e. $Cd + H_2SO_4$ (dil.) $\longrightarrow$
f. $Cd + H_2SO_4$ (conc.) $\longrightarrow$
g. $Hg + HCl \longrightarrow$
h. $Hg + H_2SO_4$ (dil.) $\longrightarrow$
i. $Hg + H_2SO_4$ (conc.) $\longrightarrow$
j. $Hg + HNO_3$ (conc.) $\longrightarrow$
k. $Hg + HNO_3$ (dil.) $\longrightarrow$

3. In Question 2, are all the acids used oxidizing acids? Have oxidation and reduction taken place in all the reactions?

4. What properties of zinc, cadmium, and mercury make their metallurgy rather simple?

5. It is said that mercury was known twenty-five hundred years ago. Why should it have been known so long before other, more abundant metals, such as zinc?

6. (*a*) Explain why a more active metal, such as zinc, is used to "protect" a less active metal, such as iron, from rusting. (*b*) Why, then, is tin used instead of zinc in making cans for storing food?

7. Explain why the addition of sodium acetate to an acidic solution of a zinc salt will permit zinc sulfide to be precipitated by hydrogen sulfide.

8. (*a*) What are some common uses of cadmium and its compounds? (*b*) What are the properties that make cadmium useful for these purposes?

9. How can *pure* mercury be obtained from cinnabar?

10. Why is a mercury meniscus inverted, that is, convex rather than concave?

11. (*a*) Why does moistened mercurous oxide decompose readily to form mercuric oxide and mercury? (*b*) What other compounds of mercury can be expected to decompose in a similar manner?

12. How could you distinguish between (*a*) zinc hydroxide and magnesium hydroxide? (*b*) zinc hydroxide and cadmium hydroxide? (*c*) corrosive sublimate and calomel?

PROBLEMS

1. One thousand kilograms of an ore containing 5 per cent of zinc sulfide was leached with sulfuric acid, and the solution so obtained was then electrolyzed. What weight of zinc should have been obtained?

2. Cinnabar was roasted and decomposed to mercury and sulfur dioxide by the reaction

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

Calculate (*a*) the pounds of ore required to make a cask (76 lb) of mercury; (*b*) the volume of 96 per cent H_2SO_4 (specific gravity, 1.84) that could be made from the SO_2.

3. A man bought 500 g of calomel, but by mistake he was given corrosive sublimate. Being a chemist he transformed it into calomel. (*a*) How could he do it? (*b*) What weight of calomel did he obtain?

CHAPTER 43

THE ALUMINUM FAMILY

General · The atoms of boron, aluminum, gallium, indium, and thallium all have three valence electrons, and hence these elements show an oxidation state of +3. Boron is a nonmetal and its hydroxide is acidic. Aluminum is a metal, but its hydroxide is amphoteric, hence the element may be found, in its compounds, either as a cation, Al^{+++}, or in the anions $Al(OH)_4^-$ or AlO_2^-.

ELEMENTS OF THE ALUMINUM FAMILY

NAME AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Boron (B)	10.82	5	2.4	2300°	2, 3
Aluminum (Al) . .	26.97	13	2.7	658°	2, 8, 3
Gallium (Ga) . . .	69.72	31	5.91	29.75°	2, 8, 18, 3
Indium (In) . . .	114.76	49	7.3	155.0°	2, 8, 18, 18, 3
Thallium (Th) . .	204.39	81	11.85	303.5°	2, 8, 18, 32, 18, 3

Boron

Boron is an acid-forming element. In its properties, as well as in those of its compounds, it strongly resembles silicon, although the formulas of the compounds of the two elements are unlike because of their difference in valence. Boron occurs in nature in boric acid (H_3BO_3) and in salts of various condensed boric acids, such as borax ($Na_2B_4O_7 \cdot 10\ H_2O$) (p. 735), which usually have very complex formulas. It constitutes only about 0.001 per cent of the earth's crust. It is used in some alloy steels and in the control rods in nuclear reactors (p. 364) to regulate the operating rates of the reactors.

Preparation and Properties · Boron is best prepared by heating the oxide, B_2O_3, with a large excess of magnesium or aluminum, which metals act not only as reducing agents but as solvents for the reduced boron:

$$B_2O_3 + 3\ Mg \longrightarrow 2\ B + 3\ MgO$$

By dissolving the excess metal with acids, the crystallized boron is obtained. Prepared in this way the product is never entirely pure. Pure crystals have been obtained by leading hydrogen and vapor of boron tribromide over a hot (1300°) wire of tungsten or tantalum. The crystals

form on the wire and are black, with metallic luster. In hardness they closely approach diamond; they have a density of 2.3 and are a very poor conductor of electricity. Boron combines with fluorine at room temperature and with the other halogens at higher temperatures. It has a great affinity for oxygen, reacting with it slowly in air, even at 100°, to form the oxide, B_2O_3, and igniting at higher temperatures. The oxide is difficult to reduce. Boron does not react with acids unless they are strong oxidizing agents like nitric or sulfuric acid, nor does it combine directly with hydrogen. With fused alkalies it dissolves to form borates.

Boric Acid (H_3BO_3) · This compound, known also as *boracic acid*, is obtained from the waters of certain hot springs, chiefly in Italy, but, more largely, by treating a hot solution of sodium tetraborate ($Na_2B_4O_7$) with sulfuric acid. Boric acid, being but sparingly soluble in cold water, crystallizes on cooling:

$$Na_2B_4O_7 + 5\ H_2O + H_2SO_4 \longrightarrow Na_2SO_4 + 4\ H_3BO_3 \downarrow$$

Boric acid crystallizes in pearly flakes which are slippery to the touch. It is a mild antiseptic and is sometimes used in medicine. Its acid properties are extremely weak. When heated to fusion, it is converted into *boric oxide* (B_2O_3).

Metaboric Acid and Tetraboric Acid · When boric acid is gently heated, it is converted into metaboric acid (HBO_2):

$$H_3BO_3 \longrightarrow HBO_2 + H_2O\uparrow$$

When metaboric acid is heated to a somewhat higher temperature, the condensed *tetraboric acid* ($H_2B_4O_7$) is formed:

$$4\ HBO_2 \longrightarrow H_2B_4O_7 + H_2O\uparrow$$

Peroxyborates · The action of peroxides on borates gives peroxyborates (also called perborates), one of the most important of which is $NaBO_3 \cdot 4\ H_2O$. This is used as an antiseptic in some tooth powders and as a mild bleaching agent.

Sodium Tetraborate ($Na_2B_4O_7$) · If we add sodium hydroxide to boric acid, we get a salt not of the simple acid but of the condensed tetraboric acid. This salt has the formula $Na_2B_4O_7$ and is called *sodium tetraborate*. If this salt is crystallized from hot water (above 60°), octahedral crystals of the hydrate, $Na_2B_4O_7 \cdot 5\ H_2O$, are obtained. If crystallized from water at ordinary temperatures, prismatic crystals are obtained, which have the formula $Na_2B_4O_7 \cdot 10\ H_2O$ and are called *borax*. This is the most important compound of boron.

Borax ($Na_2B_4O_7 \cdot 10\ H_2O$) · Borax is found native in some arid countries, as parts of California and Tibet. It is extensively used as a constitu-

ent of glass of certain kinds, and of enamels and glazes for both metal ware and pottery. It is often used in our homes to soften hard water, as a mild alkali (like washing soda, $Na_2CO_3 \cdot 10\ H_2O$), and as an antiseptic.

When borax is heated, it swells up in a sort of froth, owing to the escape of steam, and this soon melts to a clear glass. The glass has the property of easily dissolving many metallic oxides, and this fact is turned to account in working with metals. When two pieces of metal are to be joined by melting them together or by the use of some kind of solder, the surfaces must be clean and free from oxide. Brass is joined by melting borax over the joint to clean the metal, and then using a low-melting brass as a solder (brazing). Metallic oxides dissolved in melted borax often color the borax glass with characteristic tints. On this account little beads of borax are used in testing for the presence of such metals.

The reason metallic oxides dissolve in borax is that borax contains an excess of acid anhydride, as can be more easily seen if its formula is written $B_2O_3 \cdot 2\ NaBO_2$. The metallic oxide combines with this excess of acid anhydride, forming a mixed salt of metaboric acid.

Historical. Borax was highly valued by the alchemists and early metallurgists as a flux, as a mild alkali, and for medicinal purposes. It was early obtained from alkaline salt lakes in Tibet, and later it was made from the boric acid of Italian hot springs.

It was discovered in California in 1856, but in limited quantities. Years later boron minerals were found in quantity in Death Valley (California), largely as *ulexite* ($NaCaB_5O_9 \cdot 8\ H_2O$), from which borax was made, and hauled many miles to the railroad by the famous twenty-mule teams. In 1882 deposits of the crystalline rock *colemanite* ($Ca_2B_6O_{11} \cdot 5\ H_2O$) were found in several places on the edges of the Mojave Desert near the railroad, and borax production in Death Valley ceased. Still later (1913) a large deposit of *kernite* ($Na_2B_4O_7 \cdot 4\ H_2O$) was discovered in the heart of the Mojave Desert and very near the railroad. This is a soluble salt, nearly pure, and needs only recrystallization for the market.

Meanwhile the search for domestic supplies of potassium compounds led to the large-scale development of the salt beds of Searles Lake (California); in the production of potassium compounds borax is obtained as a by-product. The companies operating the kernite deposits and those of Searles Lake together produce a very large percentage of the world's boron compounds. The joint output is normally about half a million tons annually.

Other Compounds of Boron · In recent years boron trifluoride (BF_3) has become very important in industry as a catalyst for several types of reactions. Boron combines with metals to form borides, as well as with hydrogen to form hydrides in much the same manner as carbon does. For example, the following are some of the known boron hydrides: B_2H_6,

B_4H_{10}, B_5H_9, and $B_{10}H_{14}$. The bonding and valence in the boron hydrides are difficult to account for, although some progress is being made toward a satisfactory explanation. (For "boron gasoline" see page 597.)

Aluminum

Introduction · Aluminum is a newcomer among the industrial metals. Iron, copper, lead, tin, and the precious metals have been in use for ages; aluminum in the industries is the gift of the present century. The other industrial metals are all heavy bodies, but aluminum is only about one third as heavy as iron. Iron, the great structural metal of the past, rusts badly, while aluminum is little affected by air or moisture. For all purposes that require lightness, strength, and durability it is an almost ideal metal, and its late appearance in the industries was due wholly to the fact that it cannot be prepared economically by any chemical process formerly available, but had to await the electrical era for economical production. The rapid development of industries requiring light metals has intensified the interest in such metals as aluminum and magnesium. They have replaced iron for many uses; but iron will remain one of the major structural metals for years to come.

Occurrence · Next to oxygen and silicon, aluminum is the most abundant of all the elements. The free element is not found in nature, but its compounds, especially the silicates, are abundant and widely distributed, being essential constituents of all important soils and rocks except limestone and sandstone. The *feldspars*, which are the most abundant of all the minerals in the earth's crust, are silicates of aluminum and either sodium, potassium, or calcium. Since the soil has been formed largely by the disintegration of these rocks, it is rich in the silicates of aluminum, chiefly in the form of clay. Some of the other forms in which aluminum occurs in nature are the following: *corundum* (Al_2O_3); *emery* (Al_2O_3, colored black with oxide of iron); *cryolite* (Na_3AlF_6); *bauxite*, a mixture of iron oxide and hydrated aluminum oxides ($Al_2O_3 \cdot x\ H_2O$, formula uncertain) from which aluminum is prepared commercially.

Preparation · All the aluminum prepared in the United States is obtained by the electrolysis of aluminum oxide (Al_2O_3) dissolved in melted cryolite, as explained below. The oxide is prepared from bauxite, which is mined in large quantities in Arkansas; additional supplies of bauxite are imported from South America to meet our demands. The cryolite used as the solvent of the oxide is imported from Greenland or made synthetically. The process used for the production of aluminum on a

large scale is known as the Hall process, after its inventor, the American chemist Charles Hall.

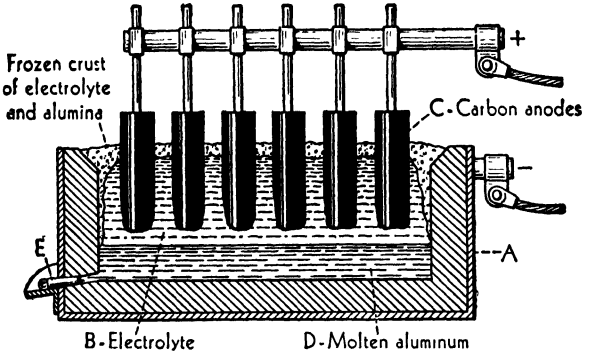


Fig. 43-1. The Electrolytic Production of Aluminum · The process is carried out in carbon-lined iron boxes, into which project carbon electrodes, *C*. The apparatus is connected with an electric generator in such a way that the carbon-lined boxes serve as the cathode and the carbon rods, *C*, as the anodes. Each box is partially filled with cryolite (or a similar artificial material), and the current is turned on, generating sufficient heat to melt the cryolite. Aluminum oxide is then added and dissolves in the liquid cryolite *as an electrolyte*. Upon electrolysis it yields aluminum and oxygen. The temperature is maintained above the melting point of aluminum, and the liquid metal, being heavier than cryolite, sinks to the bottom of the vessel, from which it is tapped off from time to time through the taphole, *E*. Part of the oxygen escapes as gas, and part of it combines with the carbon of the anodes. As the oxide is electrolyzed, more is added, so that the process is continuous

Historical. Aluminum was first prepared in relatively pure form by Oersted in 1825, by the reduction of aluminum chloride with potassium amalgam, and by Wöhler in 1827, by the reduction of the chloride with potassium. But the samples prepared in this way were for years a mere chemical curiosity for museum shelves, owing to the expense of preparation. Specimens could be procured at a cost of about $160 a pound. In 1854 the French chemist Deville substituted the metal sodium for the more expensive potassium, and within a few years the price dropped to $20 a pound. Further progress seemed then to depend upon cheaper sodium. Electrolytic sodium, developed by the American Castner, went a long way toward meeting this requirement; and for a brief period aluminum could be purchased for about $5 a pound, but by 1883 only 83 lb had been produced.

Toward the end of his course as a student in Oberlin College, young Charles Hall (Fig. 43-2) determined to solve the problem of the production of aluminum and soon became convinced that an electrolytic process was the only hope. Electrolysis of aqueous solutions was known to be a failure. Electrolysis of melted cryolite, a mineral of the formula Na_3AlF_6, found in Greenland, had been equally unsuccessful. Hall reasoned that if he could find some melted material *that would dissolve aluminum oxide*, possibly the oxide would prove to be an electrolyte in such a solution. Among other things he tried the mineral cryolite, and found that it melted easily and readily dissolved aluminum oxide.

He rigged up a number of makeshift batteries and a small furnace in a woodshed, melted the cryolite in the furnace, added aluminum oxide, and applied the current; and one morning some months after graduation he rushed over to his professor of chemistry, holding in his hands a few globules of the electrolytic metal. This was in 1886. A few months later a young Frenchman, P. L. T. Héroult, devised exactly this same process, but the Hall patents were granted priority. The large-scale process of today is essentially the same as the one devised by Hall in his woodshed.

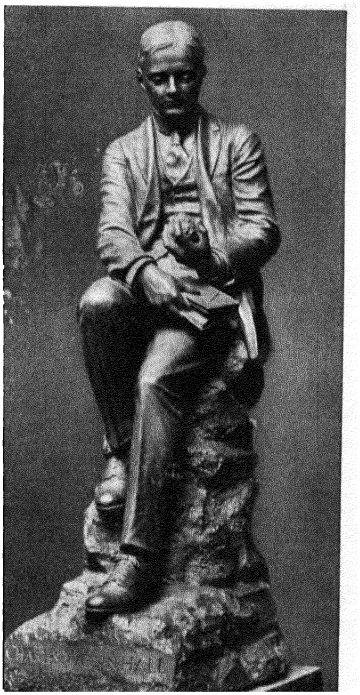


Fig. 43-2. Charles Martin Hall (1863–1914). View of an aluminum statue of Hall at Oberlin College.

Properties · Aluminum resembles tin in appearance. Its density is 2.702, and it melts at 660°. It is ductile and malleable, especially at temperatures between 100° and 150°, when it can be hammered into very thin sheets. At higher temperatures, near its melting point, it is very brittle. It is fairly hard and strong, being superior to most metals in these respects, although not equal to steel. It is an excellent conductor of heat and electricity.

Reactions · Aluminum is but slightly acted upon by water, while moist air merely dims its luster. Further action is prevented in each case by the formation of a very thin film of oxide upon the surface of the metal. It combines with many of the nonmetals, especially with the halogens and the members of the sulfur family. It is an excellent reducing agent, combining with oxygen at high temperatures, with liberation of much heat:

$$4\ Al + 3\ O_2 \longrightarrow 2\ Al_2O_3 + 2 \times 389{,}500\ cal$$

Nitric acid and dilute sulfuric acid have but little action upon it; concentrated sulfuric acid dissolves it, forming the sulfate and liberating sulfur dioxide. It reacts with hydrochloric acid:

$$2\ Al + 6\ HCl \longrightarrow 2\ AlCl_3 + 3\ H_2\uparrow$$

Aluminum resembles zinc in that it readily dissolves in strong alkalies, forming aluminates and liberating hydrogen. It is also corroded by sodium chloride, especially in the presence of oxygen and of dilute acids, such as acetic acid.

Uses · The properties of aluminum, especially when it is alloyed with suitable metals, suggest a wide variety of uses. Its lightness, strength, and resistance to corrosion adapt it to all sorts of construction purposes that range from kitchen utensils, small containers of all sorts, and innumerable small articles of daily use, to an engine base in a single casting that weighs 3800 lb. Some modern office buildings have used as much as 100,000 lb of aluminum in architectural materials roofing, cornices, window frames, and furniture; and complete walls have been constructed of aluminum sheets. Gas tanks, streetcars, and truck bodies are being made of aluminum, and the automobile and aircraft industries absorb about one third of the annual output. In a single year the washing-machine industry used over 21,000,000 lb.

For many of these purposes, as well as for many more specialized ones, alloys of aluminum are better than the pure metal; and many of these alloys contain the newer metal magnesium. For example, the very strong alloy *Duralumin* contains 4 per cent copper, 0.5 per cent magnesium, and 6 per cent manganese. It has a tensile strength equal to that of medium steel and double that of furnace aluminum. *Magnalium* is an alloy of aluminum with from 10 to 20 per cent of magnesium. An alloy is more likely to suffer corrosion by liquids than is a pure metal because of electromotive forces at the juncture of crystal particles. For this reason sheets of Duralumin and of some other alloys are sometimes coated with pure aluminum, and this combination has the trade name *Alclad.*

We have been living in a world of heavy things—heavy utensils, heavy machinery, heavy construction in buildings, heavy bridges, heavy railway coaches, and heavy automobile bodies. Our construction metals have averaged between 7.5 and 8.5 in density. We are moving into an age which demands that all these things shall be lighter in weight, with the aircraft as the shining example. So wherever it is possible, we are turning to aluminum, one third as heavy as iron, and to magnesium, one fourth as heavy. These metals or their alloys can be brought into forms that are as hard, strong, malleable, and ductile as steel and as resistant to corrosion, and that are as good electrical conductors as copper or better than copper, weight for weight. (In fact, aluminum wire is coming into extensive use for electric-power transmission lines.) The annual production of aluminum in the United States in 1954 was about 1,450,000 tons; and that of magnesium about 80,000 tons, though both figures depend on industrial conditions. The price of aluminum has been 20–26 cents a pound, and that of magnesium 24–33 cents.

The Light Metals as Gas-absorbers and Metal-purifiers · In making high-vacuum tubes, such as radio, X-ray, or thermionic tubes, one of the great problems has been to remove the last traces of the original atmospheric gases, chiefly oxygen, nitrogen, and water vapor. To accomplish this removal, a small pellet of one of the very active metals is placed in the tube before it is evacuated; and

after the tube is sealed, the pellet in the tube is heated. Nearly any one of the alkali or alkaline-earth metals, as well as magnesium or aluminum, will combine energetically with these residual gases to form solid products and improve the vacuum.

In a similar way the alkaline-earth metals or magnesium or aluminum are sometimes melted with heavy metals, such as iron or nickel, as they are poured. The active metals take away any trace of oxygen, nitrogen, or sulfur remaining in the less active metal, and the products formed pass off to the surface of the metal, leaving it free of blowholes or particles of oxides. Metals used for this purpose are called *scavengers*, or purifiers, and this is one of the large uses of both aluminum (for iron) and magnesium (for nickel).

Goldschmidt reduction and welding process. Aluminum has a great affinity for oxygen and is able to reduce the oxides of many metals that are difficult to reduce by other means, such as those of manganese or chromium (p. 606). A great deal of heat is set free in such reductions, and this fact was turned to account in the process of welding iron by the German chemist Goldschmidt. The iron joint to be welded is cleaned and heated with a gasoline torch. A mixture of iron oxide (Fe_2O_3) and finely divided aluminum is prepared, often with the addition of an oxidizing agent, such as barium peroxide (BaO_2), to increase further the heat. This mixture, called *Thermit*, is placed in a funnel-shaped clay crucible immediately over the joint (*B*, Fig. 43-3), and the reduction of the iron oxide by the aluminum is started by igniting a primer wire of magnesium. The white-hot iron is then allowed to flow into a form surrounding the joint to make the weld (*A*, Fig. 43-3). Electrical welding has largely replaced this Thermit process except in special cases.

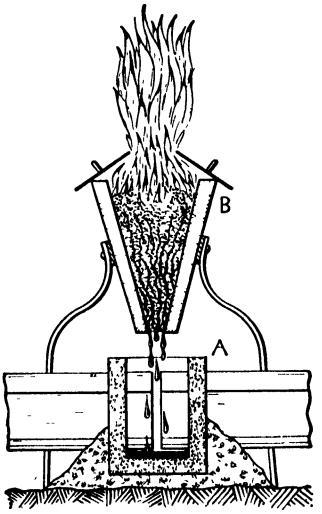


Fig. 43-3. Welding Car Rails with Thermit

Compounds of Aluminum · Aluminum is a trivalent metal, and the formulas of its anhydrous compounds therefore resemble those of bismuth and antimony. Aluminum hydroxide, like antimony hydroxide, is amphoteric. With strong bases it forms aluminates, such as sodium aluminate ($NaAlO_2$), derived from the partial anhydride $AlO \cdot OH$, while with acids it forms salts, such as the chloride, $AlCl_3$, and the sulfate, $Al_2(SO_4)_3$. These salts are characterized by their great tendency to undergo hydrolysis. Aqueous solutions of the chloride and sulfate are acid in reaction, while the carbonate and sulfide are completely decomposed by water.

Aluminum Oxide (Al_2O_3) · This compound is found in nature as the relatively pure colorless mineral *corundum*, and as *emery* when colored brown or black with iron oxide. In transparent crystals, tinted with ox-

ides of various metals, such as chromium, titanium, cobalt, iron, and manganese, it is a precious gem stone, and includes ruby (red), sapphire (blue), Oriental topaz (yellow), and Oriental amethyst (violet). All these varieties are almost as hard as diamond, and the cheaper ones, corundum and emery, are used as abrasives. The pure oxide is obtained as a white powder by heating the hydroxide:

$$2\ Al(OH)_3 \longrightarrow Al_2O_3 + 3\ H_2O$$

By heating the impure natural hydroxide (bauxite) an abrasive is produced that is superior to the natural oxide and is sold under various trade names, such as *Alundum* and *Aloxite*. Some forms of firebrick, and crucibles and tubes for laboratory use, are made from these materials.

Artificial Gems · Aluminum oxide can be melted in oxyhydrogen furnaces, and obtained in crystalline form. The pure colorless gem so produced is called white sapphire; by adding the requisite metallic oxide almost any desired color can be given the gem stone. The rubies and sapphires so produced are identical in almost every respect with the natural stones and are artificial gems, not imitation ones.

Abrasives · Abrasives are hard substances easily powdered to grains of various sizes, and used for grinding and polishing purposes. Sandpaper and emery paper are familiar examples. Many machine parts, such as the valves of an automobile engine, must be accurately fitted by grinding; and the demand for harder and harder abrasives increases with the hardness of materials used in machines. Artificial abrasives have largely displaced the natural ones, and the artificial oxides of aluminum, together with hard carbides, such as Carborundum (p. 488), are examples of the newer abrasives.

Aluminum Hydroxide ($Al(OH)_3$) · As we have seen, this hydroxide, in a partially dehydrated form, constitutes the mineral bauxite and is the chief ore of aluminum. It is a very weak base and is therefore amphoteric, and its salts are extensively hydrolyzed in solution. It forms a colloidal jelly, which has high adsorptive properties; for this reason the colloidal hydroxide in solutions of various kinds is important in water purification and in dyeing. When aluminum hydroxide is dried, it changes into a porous oxide, which is much used as a catalyst in many reactions.

Aluminum hydroxide is soluble in strong alkalies, forming metaluminates, such as $NaAlO_2$. The name *spinels* is given to the naturally occurring metaluminates of bivalent metals and to similar compounds, such as

Spinel	$Mg(AlO_2)_2$, or $MgO \cdot Al_2O_3$
Franklinite	$Zn(FeO_2)_2$, or $ZnO \cdot Fe_2O_3$
Magnetite	$Fe(FeO_2)_2$, or $FeO \cdot Fe_2O_3$
Chromite	$Fe(CrO_2)_2$, or $FeO \cdot Cr_2O_3$

Calcium aluminate ($Ca(AlO_2)_2$) is an important constituent of cement.

Aluminum Sulfate ***($Al_2(SO_4)_3$)*** · This compound is prepared commercially by the action of sulfuric acid on either bauxite or kaolin. The latter is a silicate of aluminum occurring abundantly in nature. The sulfate crystallizes from water in a variety of hydrates, the usual one having the composition expressed by the formula $Al_2(SO_4)_3 \cdot 18\ H_2O$. It is the cheapest of the soluble salts of aluminum and is therefore the one most largely used when a salt of this metal is desired. Its principal uses are in the manufacture of alum and paper, in the purification of water, and as a mordant in dyeing.

Alums · Aluminum sulfate has the property of combining with the sulfates of the alkali metals to form compounds called *alums*. Thus, with potassium sulfate the reaction is expressed by the equation

$$K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O \longrightarrow 2\ KAl(SO_4)_2 \cdot 12\ H_2O$$

The sulfates of some other trivalent metals form similar compounds with the alkali sulfates, and these compounds are also called alums, though they contain no aluminum. They all crystallize in octahedra and contain 12 molecules of water of hydration. The alums most frequently prepared are the following:

Potassium alum	$KAl(SO_4)_2 \cdot 12\ H_2O$
Ammonium alum	$NH_4Al(SO_4)_2 \cdot 12\ H_2O$
Ammonium iron alum	$NH_4Fe(SO_4)_2 \cdot 12\ H_2O$
Potassium chrome alum	$KCr(SO_4)_2 \cdot 12\ H_2O$

Since the alums crystallize so readily, it is easy to obtain them in pure condition. For this reason the aluminum alums were long used in place of aluminum sulfate, which is difficult to purify. Improved processes have been devised for preparing the latter compound cheaply and in pure condition, so that now it has largely replaced alum for many commercial uses, such as the purification of water. In commerce the word *alum* is often used, at present, to denote aluminum sulfate. The alums are used in the manufacture of paper, in water purification, and as mordants in dyeing. Smaller quantities are used in baking powders and in certain foods, such as pickles, to make them more crisp.

Aluminum Chloride ***($AlCl_3$)*** · This compound is made by passing dry chlorine or hydrogen chloride though a heated tube containing aluminum. It is a white solid which sublimes without melting under atmospheric pressure, and melts under increased pressure at 194°. In the vapor state its molecules have the formula Al_2Cl_6. It is strongly hygroscopic and fumes when exposed to the air, owing to the formation of hydrochloric acid through the action of moisture. The hexahydrate is formed by dissolving aluminum hydroxide in hydrochloric acid and evaporating to crystallization. When heated, the hydrate is decomposed, forming aluminum oxide and water, so that the anhydrous compound cannot be prepared directly from the hydrate. The anhydrous compound is a good catalyst in certain reactions in organic chemistry; it has been used also as a catalyst in the "cracking" of petroleum (p. 517).

Aluminum Sulfide (Al_2S_3) · The sulfide is prepared by heating a mixture of aluminum and sulfur to a high temperature. It may be obtained either as a black mass or as a yellow crystalline solid. It is completely hydrolyzed upon the addition of water:

$$Al_2S_3 + 6\ H_2O \longrightarrow 2\ Al(OH)_3\downarrow + 3\ H_2S$$

When a soluble sulfide, such as sodium or ammonium sulfide, is added to a solution of an aluminum salt, aluminum sulfide may be formed; but if formed it is immediately hydrolyzed, so that the precipitate obtained consists of aluminum hydroxide. The complete reaction is represented by the following equation:

$$3\ Na_2S + 2\ AlCl_3 + 6\ H_2O \longrightarrow 2\ Al(OH)_3\downarrow + 6\ NaCl + 3\ H_2S$$

Aluminum Nitride (*AlN*) · This compound is prepared by direct union of aluminum and nitrogen at a high temperature. It derives its chief interest from the fact that when it is treated with steam, ammonia is formed:

$$2\ AlN + 3\ H_2O \longrightarrow Al_2O_3 + 2\ NH_3\uparrow$$

The nitrogen used in preparing the nitride is obtained from the air. It is possible, therefore, through the intermediate formation of aluminum nitride, to convert the nitrogen from the air into ammonia (p. 398).

Aluminum Carbide (Al_4C_3) · This compound was obtained by Moissan by heating aluminum oxide with carbon in an electric furnace. Its chief interest lies in the fact that it reacts with water to form methane:

$$Al_4C_3 + 12\ H_2O \longrightarrow 4\ Al(OH)_3 + 3\ CH_4\uparrow$$

Since methane constitutes nearly 90 per cent of natural gas, it has been suggested that the latter product may, in some cases at least, have resulted from the action of water upon the carbides formed when the crust of the earth was in a molten condition.

Hydrolysis of Salts of Aluminum · Although aluminum hydroxide forms fairly stable salts with strong acids, it is such a weak base that its salts with weak acids are readily hydrolyzed (p. 457). Thus, when an aluminum salt and a soluble carbonate are brought together in solution, we might expect to have aluminum carbonate formed, in accordance with the equation

$$3\ Na_2CO_3 + 2\ AlCl_3 \longrightarrow Al_2(CO_3)_3 + 6\ NaCl$$

But if it is formed at all, it instantly hydrolyzes. The products of the hydrolysis are aluminum hydroxide and carbonic acid, the latter then forming carbon dioxide and water:

$$Al_2(CO_3)_3 + 6\ H_2O \longrightarrow 2\ Al(OH)_3\downarrow + 3\ H_2CO_3$$
$$3\ H_2CO_3 \longrightarrow 3\ H_2O + 3\ CO_2\uparrow$$

It is because of these reactions that an alum is used as a constituent of some baking powders.

Baking Powders · Every baking powder contains three ingredients, the names and functions of which are as follows: (1) sodium bicarbonate to furnish the carbon dioxide; (2) some compound which, in the presence of water, reacts with the bicarbonate and slowly liberates carbon dioxide; (3) starch or flour, which serves to dilute the powder to the desired strength (not less than 12 per cent of available carbon dioxide) and at the same time prevents the powder from deteriorating by absorbing any moisture present. The compounds used for liberating the carbon dioxide are the following: (1) potassium acid tartrate, commonly known as cream of tartar; (2) tartaric acid; (3) calcium dihydrogen phosphate; (4) sodium aluminum sulfate (often designated as S.A.S.). Often certain mixtures of two of these compounds are used; thus, almost all cream of tartar baking powders also contain tartaric acid. The equations for the reactions that take place between sodium bicarbonate and each of the compounds given above are as follows:

Potassium acid tartrate (cream of tartar):

$$KHC_4H_4O_6 + NaHCO_3 \longrightarrow KNaC_4H_4O_6 + H_2O + CO_2\uparrow$$

Tartaric acid:

$$H_2C_4H_4O_6 + 2\ NaHCO_3 \longrightarrow Na_2C_4H_4O_6 + 2\ H_2O + 2\ CO_2\uparrow$$

Calcium dihydrogen phosphate:

$$Ca(H_2PO_4)_2 + 2\ NaHCO_3 \longrightarrow CaHPO_4 + Na_2HPO_4 + 2\ H_2O + 2\ CO_2\uparrow$$

It is probable that other reactions than the one just given take place in the case of the phosphate powders, but this is the principal one.

Sodium aluminum sulfate:

$$NaAl(SO_4)_2 + 3\ NaHCO_3 \longrightarrow Al(OH)_3 + 2\ Na_2SO_4 + 3\ CO_2\uparrow$$

Aluminum Silicates · The silicates of aluminum are widely and abundantly distributed. Sometime in the history of the earth's formation its surface must have been composed of a solid igneous rock formed by the cooling of the molten mass. The various silicates of aluminum constitute by far the largest percentage of these igneous rocks. Most important of these are the *feldspars*, known as *orthoclase* ($KAlSi_3O_8$), *albite* ($NaAlSi_3O_8$), and *microcline*, which has the same chemical composition as orthoclase but is different in crystalline structure. The gradual disintegration, or weathering, of these rocks through various agencies, such as the action of air and water, has resulted in the formation of the mineral constituents of the soil. The changes taking place in the process are often very complex and are not well understood. Thus, in the weathering of orthoclase the potassium is removed, together with a portion of the silica, while at the same time water enters into chemical combination with the residue. In this way there is formed the soft, plastic mineral known as *kaolin* or *kaolinite* ($Al_2Si_2O_7 \cdot 2\ H_2O$, often written $Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O$). Large

quantities of this mineral are sometimes found deposited in beds in fairly pure form. More often it has been carried away by running water and mixed with various other products resulting from the crushing and weathering of rocks, especially silica (sand) and compounds of iron, calcium, and magnesium, in this way forming the product known as *clay*. It is evident, therefore, that clay is extremely variable in composition, though the essential constituent appears to be kaolin. *Fuller's earth* is a name given to certain clays that possess the property of decolorizing and otherwise purifying fats and oils. *Bentonite* is a special type of clay mined in South Dakota; it has varied uses.

Ultramarine · The mineral known as *lapis lazuli* has long been known and highly prized because of its beautiful blue color. The powdered mineral was used by the ancients as a color pigment, called *ultramarine*. This name is now applied to the artificial product prepared by heating together, under suitable conditions, kaolin, charcoal, sodium carbonate, sodium sulfate, and sulfur. The product so obtained is very similar in composition and properties to the natural product and is much less expensive. By suitable variation of the method of preparation and of the ingredients employed, a variety of tints may be obtained. It is a very complex substance, and its exact composition is not known with certainty. The color seems to be due to the presence of colloidal sulfur. Large quantities of it are used as a pigment, especially in wall papers.

Gallium, Indium, and Thallium

The other members of the aluminum family (gallium, indium, and thallium) are elements of rare occurrence in nature and were discovered by spectroscopic study of various minerals. They have brilliant and characteristic spectrum lines, and through these are known to be widely distributed in certain classes of minerals; with the exception of a few rare ores of thallium, however, they have never been found to an extent of more than about 0.1 per cent in any mineral. Like aluminum, they are trivalent in their best-known compounds, but each of them forms at least one series of salts in which it is univalent or bivalent as well. All three metals would find many uses if they were more available.

Gallium · Gallium was discovered in certain zinc blendes by the Frenchman Lecoq de Boisbaudran in 1875, and named in honor of his country, the Latin name for which is *Gallia*. It is found in ores of zinc, aluminum, copper, and iron, and in the pig iron from a few iron ores. At present the most productive source is certain residues from distilled zinc. These are estimated to contain from 3 to 5 oz of gallium to the ton. Traces of it are nearly always present in bauxite. It is a shining white

metal of very low melting point (29.7°). In addition to the usual series of salts, in which it is trivalent, it forms a second series, in which it is bivalent.

Indium · This metal was discovered in a specimen of Freiburg zinc blende by Reich and Richter in 1863, while they were examining it spectroscopically for thallium. It is a constituent of certain zinc ores found in our Western states but is present only in very small percentages. In 1924 the world's supply consisted of one gram and was valued at $10. Today the potential supply is much greater, and the price has been reduced to such an extent (to about $2 per ounce) that the metal may find commercial uses. It is a white, lustrous metal, resembling zinc and aluminum. It melts at 155°, and its density is 7.3. In addition to salts resembling those of aluminum, it forms two other series, in one of which it is bivalent and in the other univalent. The oxide In_2O_3 imparts a yellow color to glass.

Thallium · Thallium is by far the most abundant of these three elements. It was discovered by Crookes in 1861 in the slimes from the lead chamber of a sulfuric acid factory. The name was suggested by its brilliant green spectrum line (*thallium* being derived from a Greek word meaning "a green twig"). It frequently accompanies the sulfides of the heavier metals, such as copper, lead, iron, and zinc, and is obtained from the flue dusts which are formed in the roasting of such sulfides. It is chiefly obtained at present as a by-product in the refining of cadmium. To some extent it also accompanies potassium and has been found in carnallite. It is a heavy metal (density, 11.85) and is softer than lead, which it very much resembles in appearance. It melts at 303°. It finds a limited use in certain alloys, but its chief use (as the sulfate Tl_2SO_4) is as a poison for ants and rats.

Its chemical properties are very interesting. As a trivalent element, it forms salts which resemble those of aluminum in a general way, though its hydroxide is rusty red in color, like ferric hydroxide, and its sulfide, Tl_2S_3, is soluble in ammonium sulfide, like the sulfides of arsenic and antimony. As a univalent element, it forms a hydroxide, TlOH, which is a *strong, soluble* base like potassium hydroxide, and its salts are, as a rule, very similar to those of potassium. Its chloride and cyanide, however, are insoluble in water and acids, resembling the corresponding salts of silver in this respect.

QUESTIONS

1. Define and, where possible, illustrate by an example each of the following: (*a*) *condensed acid*; (*b*) an *alum*; (*c*) a *baking powder*; (*d*) *amphoteric hydroxide*; (*e*) *hydrolysis*; (*f*) a *spinel*.

2. What are the common uses (*a*) of boron? (*b*) of borax? (*c*) of the metaborates? (*d*) of boric acid?

3. (*a*) Outline the steps in the history of the development of aluminum production. (*b*) Describe in detail the modern electrolytic process.

4. Since aluminum is used for cooking vessels, it would seem not to be acted on by water. Why, then, can it not be prepared by the electrolysis of the aqueous solution of its salts?

5. (*a*) In addition to aluminum hydroxide, what other hydroxides are amphoteric? (*b*) How do you explain the fact that amphoteric hydroxides are always *very weak* acids and bases?

6. When aluminum hydroxide is precipitated it forms a colloidal, jellylike substance (much like silicic acid in appearance); when an attempt is made to dry it, it loses water continuously so as to have any composition between $Al(OH)_3$ and Al_2O_3. Account for these phenomena in terms of the structure of the precipitate.

7. In addition to aluminum, what other elements or compounds have we found to combine directly with nitrogen?

8. (*a*) Why should aluminum sulfate displace alum for commercial purposes? (*b*) Would it serve in place of alum in a baking powder?

9. Make a comprehensive comparison of the uses of aluminum, magnesium, and zinc, and explain the advantages of using these metals.

PROBLEMS

1. Five hundred grams of feldspar ($KAlSi_3O_8$) was powdered and, by the addition of sulfuric acid, converted into crystallized potassium alum. What weight of alum could be obtained theoretically?

2. What is the percentage of water of hydration in (*a*) crystallized aluminum sulfate? (*b*) potassium alum?

3. What volume of carbon dioxide (under standard conditions) could be obtained from a weight of calcium acid phosphate baking powder containing 100 g of calcium dihydrogen phosphate (together with sodium bicarbonate)?

4. Five hundred grams of aluminum was heated in an atmosphere of nitrogen to the completion of the reaction, and the product was then treated with hydrochloric acid. What weight of ammonium chloride was obtained?

5. What *relative* weights of sodium, zinc, cadmium, and aluminum will be required to yield the same volume of hydrogen by action on water or on acids? (Take sodium as unity for comparison.)

CHAPTER 44

GERMANIUM, TIN, AND LEAD

Introduction · The three heavier members of the carbon family—germanium, tin, and lead—differ from carbon and silicon (1) in the size of their atoms, (2) in the number of electron shells between the nucleus and the valence shell, and (3) in the fact that the electron shell just below the valence shell has eighteen electrons. As a result, in spite of their higher nuclear charge, the valence electrons are less firmly attracted to the nucleus. Two of these electrons are readily ionizable, and all four may be used in formation of covalent bonds. Hence these elements show

ELEMENTS OF GROUP IVB					
NAME AND SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Carbon (C) . .	6	12.01	2.25 (graphite)	3500° (graphite)	2, 4
Silicon (Si) . .	14	28.06	2.4	1427°	2, 8, 4
Germanium (Ge)	32	72.60	5.36	958°	2, 8, 18, 4
Tin (Sn) . . .	50	118.70	7.31	232°	2, 8, 18, 18, 4
Lead (Pb) . . .	82	207.22	11.34	328°	2, 8, 18, 32, 18, 4

oxidation states of $+2$ and $+4$, and an electrovalence of $+2$, and occasionally an electrovalence of $+4$. They are therefore metallic in some of their compounds, forming bivalent, positively charged ions in the presence of strong acids. The hydroxides in the oxidation state of $+2$ are amphoteric. In the oxidation state of $+4$ the elements are principally nonmetals, forming acids whose formulas resemble those of the corresponding acids of carbon and silicon.

Germanium

Germanium was discovered in 1886 by Winkler, in connection with some analyses of the rare mineral *argyrodite*. His analyses failed to account for from 6 to 7 per cent of the mineral, and a long and careful search resulted in the discovery of the new element. It was found to fulfill in a remarkable way the predictions of Mendeleev for the properties of an undiscovered element which should follow silicon in Group IVB, and which he provisionally named ekasilicon. It occurs in exceedingly small percentages in many American zinc ores (0.01 per cent), and the residue

from zinc stills is the chief source of the element. Germanium is a brittle, crystalline, metallic substance which has a density of 5.36 and melts at 958.5°. An important use is in making transistors for electronic equipment. It forms two oxides, of the formulas GeO and GeO_2, each of which is amphoteric in character. Its compounds resemble those of tin.

Tin and Lead

Historical Introduction · Tin and lead are two of the six metals known to the ancient world, though neither metal is found in the free state to any appreciable extent. Objects of tin-bronze date back more than five thousand years. Tin was long confused with lead and was sometimes called white lead. The distinction between the two metals was first clearly indicated in the writings of Pliny in the first century A.D. Tin was later called *stannum*, whence the names *stannous* and *stannic* and the symbol Sn.

Articles made of lead have been found in ruins of great antiquity, and the metal was evidently in common use in very early times. The Romans called it *plumbum* (which gives us the symbol Pb) and used it for water pipes, much as we do today.

Occurrence · Tin is found chiefly as the oxide, SnO_2, called tinstone, or *cassiterite*; this is its only metallurgical ore. Until the thirteenth century tin was apparently obtained from Cornwall (England), but at present Bolivia, the Belgian Congo, and Nigeria stand first in production, followed by the Malay States and Siam. Tin is one of the few metals of industrial importance not found to any extent in the United States. The production of the United States is less than 100 tons; yet it uses from one third to one half of all the tin mined in the whole world, which ranges between 100,000 and 200,000 tons annually. By far the larger part of the metallic tin used in the United States is obtained by the domestic smelting of imported ores.

In contrast with its small contribution of tin, the United States leads all other countries, with 317,000 tons, in the world's output of lead (1954); and the chief mining states are Missouri, Idaho, and Utah. Australia, Mexico, and Canada rank next to the United States. The minerals of most value to the metallurgist are *galenite* (galena), PbS, and to a less extent *cerussite* ($PbCO_3$) and *anglesite* ($PbSO_4$). The price of lead is 15 to 20 cents per pound, as compared with from 80 cents to $1.20 per pound for tin. Next to iron, and possibly aluminum and magnesium, lead is our cheapest metal.

Metallurgy · The metallurgy of tin depends on an *oxide* reduction

similar to that of iron; the metallurgy of lead is a *sulfide* reduction like that of copper. The chief impurities of tin oxide ores are sulfides of copper and iron, together with small percentages of arsenic. The ore is first concentrated (usually by flotation) and is then roasted in air to drive off all arsenic as volatile oxide and to convert the sulfides into soluble sulfates. The sulfates are washed out with water or dilute acids, a flux of limestone and silica is added to the ore, and the tin oxide is reduced by carbon:

$$SnO_2 + 2\,C \longrightarrow Sn + 2\,CO\uparrow$$

The ores of lead are chiefly *sulfides*, usually associated with more or less silver sulfide and often a little gold; silver ores are often purposely added to silver-bearing lead ores and the two metals smelted together. When no silver is present, the ores are roasted in air in an open oven until they are partially oxidized to form a mixture of sulfide, sulfate, and oxide of lead. Access to air is then shut off and the temperature raised to bring about the following reactions:

$$PbS + 2\,PbO \longrightarrow 3\,Pb + SO_2\uparrow$$
$$PbS + PbSO_4 \longrightarrow 2\,Pb + 2\,SO_2\uparrow$$

Silver-bearing ores are worked at a higher temperature in a blast furnace the bottom of which consists of a large crucible-like structure made of firebrick. The roasted ore is charged into the furnace along with coke and a flux consisting of limestone and iron ore. The chief reactions that produce lead (and silver) are these:

$$PbS + FeO + C \longrightarrow Pb + FeS + CO\uparrow$$
$$PbSO_4 + FeO + 5\,C \longrightarrow Pb + FeS + 5\,CO\uparrow$$

The liquid lead, carrying the silver and gold in solution together with varying percentages of copper, antimony, bismuth, and arsenic, collects in the crucible and is tapped off.

Refining of Lead · The lead from the blast furnace is *hard* because of the metals alloyed with it. It is refined (softened) by a number of methods, largely by the two following ones:

1. **The Parkes method.** The impure lead is heated just to its melting point and kept at this temperature for several days. Copper is but slightly soluble in lead at this temperature, and rises to the surface and is skimmed off. The lead is then heated to a higher temperature during a number of days for the air to oxidize the arsenic, antimony, and bismuth present. These oxides form a scum (*dross*) on the surface of the lead and are removed. The lead is then transferred to a huge kettle, in which it is kept melted; then a small percentage of zinc is added, and the liquid metal is thoroughly stirred. Gold, silver, and copper are

much more soluble in zinc than in lead, and zinc is little soluble in lead. As a result of these differences in solubility, as soon as the stirring ceases the zinc rises to the surface of the lead, together with the other metals dissolved in it. When the temperature is lowered, the zinc alloy forms a solid crust, which is removed; and the operation is repeated until all the precious metals have been extracted from the lead.

The zinc crusts are distilled from a retort, and the zinc is recovered to be used again. The residue contains the gold and silver. Some zinc remains in the lead, and this is removed either by oxidation or by converting it into the chloride by treatment with chlorine.

2. **The electrolytic process (Betts process).** In this process impure lead is used as the anode in a cell in which the electrolyte is fluosilicic acid and lead fluosilicate ($PbSiF_6$). Pure lead is deposited on the cathode, and the precious metals are recovered from the spent anode plates and the electrolytic muds.

In both these processes the silver is parted from the gold of the residues, as explained in connection with silver (p. 713).

Properties of the Metals · As we ordinarily see it, tin is a silver-white metal, harder than lead and fairly malleable. It is a low-melting metal and is slightly lighter than iron. Lead is a heavy, silvery metal and is the softest of the industrial heavy metals. It is malleable, has little strength, and is a moderately good conductor of electricity. It crystallizes in the isometric system.

It is of interest that tin occurs in three allotropic forms, which pass into one another at definite transition temperatures:

$$\text{Gray tin} \overset{(18°)}{\rightleftarrows} \text{tetragonal} \overset{(161°)}{\rightleftarrows} \text{rhombic} \overset{(231.85°)}{\rightleftarrows} \text{liquid}$$

The first of these transitions is especially interesting because it takes place at ordinary temperatures. Below 18° ordinary white tin (tetragonal) is in an unstable state and under some conditions changes into the gray form; at the same time it loses its metallic appearance and crumbles to a powder.

Tin Plague · The transformation of white tin into the gray form is sometimes a serious matter (Fig. 44-1). It was first noticed in connection with the deterioration of some organ pipes made of tin, which developed holes and then broke up completely. Later, ingots of tin stored in a Russian customhouse during a very cold winter were found to have crumbled to powder. When the transformation once starts, it continues to spread as long as the temperature is below 18°, and this uncontrollable spread has been called the tin plague or museum disease, since it sometimes spreads over tin objects in a cold museum. The speed of the transformation is increased by contact with a solution of certain salts in which tin is slightly soluble.

Chemical Properties of the Metals · In the electrochemical series tin and lead are close together just above hydrogen, and we should expect

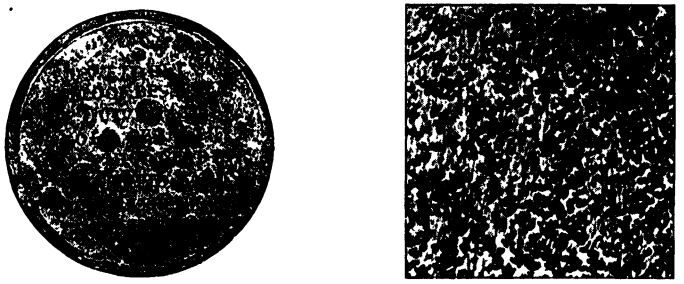


Fig. 44-1. Tin Objects in a Museum, Showing the Transformation of White Tin into the Gray Form (Museum Disease)

them to have very similar chemical properties. Their similarity is somewhat disguised by the fact that many simple compounds of lead are insoluble and form protective coverings on the surface of the metal. Tin slowly reacts with both hydrochloric and dilute sulfuric acids, with evolution of hydrogen; but lead quickly becomes covered with a protective film of lead chloride or sulfate. Tin is not perceptibly affected by air or water at ordinary temperatures, while a film of oxide forms on the surface of lead, changing its silvery luster to a dull blue-gray, and finally forms a thicker covering of white basic carbonate. Soft water containing dissolved oxygen acts on lead to form the somewhat soluble lead hydroxide, $Pb(OH)_2$.

Weak acids, such as acetic acid, act on lead more readily than on tin. Acids such as nitric acid or concentrated sulfuric acid oxidize tin to an insoluble hydrate of the oxide SnO_2, while they act on lead as they do on copper (p. 404) to form lead nitrate or lead sulfate. Strong alkalies act on both metals as they do on zinc (p. 723). For example:

$$Sn + 2\,OH^- + 2\,H_2O \longrightarrow Sn(OH)_4^{--} + H_2\uparrow$$

All compounds of lead are poisonous and tend to accumulate in the system, and all workers with the metal of its compounds must use precautions against lead poisoning.

Uses of the Metals · The important uses of tin and lead as metals depend largely on their resistance to more than superficial corrosion and on their value in alloys.

More than one third of the tin imported into the United States is used in making tin plate by dipping sheet steel into melted tin (see rusting of iron, p. 635) or by electroplating the tin on the steel. The steel is strong and cheap, and the tin gives resistance to corrosion. The large uses of

tin plate are for making tin cans, roofs, and cooking vessels. Tinned copper is sometimes used for this last purpose. Pure tin pipes of small size are used for conveying pure water in laboratories. Lead water pipes have long been used because they are flexible and easily installed. With any ordinary water the interior of the pipe quickly becomes covered with a protective coating of basic carbonate or sulfate. With rain water or other very soft water enough lead passes into solution as hydroxide to be a threat to health. Iron pipes have largely taken the place of lead ones. The condensing chambers of sulfuric acid plants are covered with sheet lead (p. 386) to resist corrosion by the dilute acid that collects in the chambers. Architectural devices, such as the mullions and "leads" between glass panes in windows, are often made of nearly pure lead.

The second great use of tin and lead is in making alloys. Many of these, such as bronze, bearing metals, low-melting metals, and some brasses, have been described in connection with copper and other metals. *Soft solder* and pewter are essentially alloys of tin and lead, though the latter usually contains some antimony to harden it. *Type metal* consists of the same three metals. Tin foil often contains some lead; it has been largely replaced by aluminum foil and cellophane. The greatest use of lead is for making storage batteries. The supporting grid of the battery plates is a lead-antimony alloy. The sheathing for the protection of electric cables is either lead itself or an alloy of lead with variable percentages of calcium and barium. This alloy, called *Frary metal*, is made by electrolyzing a fused mixture of the chlorides of calcium and barium, with the use of a liquid lead cathode, in which the depositing metals dissolve. Shot is an alloy of lead and a very small percentage of arsenic. A great many bearing metals and antifriction metals contain lead as a component.

Rusting of Tin Plate · If the coating of tin on tin plate is scratched through to the steel, the steel will rust faster than if there were no tin covering. The two metals and the water constitute a battery much like the Daniell cell (p. 223), and in a battery the metal highest in the electrochemical series is the one that is corroded. In the case of galvanized iron the zinc corrodes first, and the iron resists rusting as long as any zinc is present.

Soldering and Brazing · The use of solder in joining two metal surfaces depends upon (1) the low melting point of the solder and (2) the fact that it flows over *clean* metal surfaces and sticks to them on cooling. To secure clean surfaces free from oxide a suitable flux must be used, which will either *dissolve* the oxide as fast as it forms or *reduce* it again to metal or float it away. The usual fluxes are zinc chloride, ammonium chloride, rosin, and stearin. In *brazing*, or *hard-soldering*, the process is essentially the same, except that a low-melting brass is used instead of solder, and borax is used as a flux.

Compounds of Tin and Lead · In practically all their compounds tin and lead act either as bivalent or as tetravalent elements. When they act as bivalent metals, their compounds are designated as *stannous* and *plumbous*; as tetravalent metals, they form *stannic* and *plumbic* compounds. Lead is rarely tetravalent, and the bivalent compounds are referred to merely as lead compounds.

The Oxides · Stannous oxide (SnO) can be obtained as a black powder by heating stannous oxalate (SnC_2O_4); but it is rarely prepared. Lead oxide (PbO), called *litharge*, is made by heating lead in a current of air or by heating the carbonate. It is a by-product in cupeling silver-lead alloys (p. 713). In color it ranges from yellow or light brown to orange, depending on the way in which it is made. The light-brown form is called *massicot*. Its chief use is in making paints, glass, glazes, and other compounds of lead. Mixed with glycerin it forms a cement useful for joining glass and stone.

Tin dioxide (SnO_2) is the chief mineral ore of tin. By burning tin in air or by treating it with nitric acid and heating the resulting hydrated oxide, it is obtained as a white powder. It is used in making opaque glass and enamels. Plumbic oxide (PbO_2), usually called *lead dioxide*, is a dark-brown powder. It is obtained by the action of bleaching powder on sodium plumbite (Na_2PbO_2):

$$Na_2PbO_2 + Ca(OCl)Cl + H_2O \longrightarrow 2\ NaOH + CaCl_2 + PbO_2\downarrow$$

It forms a brown coating on the anode when solutions of lead salts are electrolyzed, and is the active material on the anodes of storage batteries (p. 227). It is a good oxidizing agent. For example, with hydrochloric acid it acts much like manganese dioxide and evolves chlorine:

$$PbO_2 + 4\ HCl \longrightarrow PbCl_2 + 2\ H_2O + Cl_2\uparrow$$

The Hydroxides · The hydroxides of tin and lead, in both oxidation states, are amphoteric in character. They form salts with both acids and bases. When stannous chloride or lead nitrate is treated with sodium hydroxide, the hydroxide of either metal is at first precipitated as a white amorphous gel. For example:

$$SnCl_2 + 2\ NaOH \longrightarrow 2\ NaCl + Sn(OH)_2\downarrow$$

Excess hydroxide ions causes these precipitates to dissolve (as with zinc hydroxide) to form salts (or complex ions). For example:

$$Sn(OH)_2 + OH^-(\text{excess}) \longrightarrow Sn(OH)_3^- \text{ or } (HSnO_2^- + H_2O)$$
$$Pb(OH)_2 + OH^-(\text{excess}) \longrightarrow Pb(OH)_3^- \text{ or } (HPbO_2^- + H_2O)$$

The resulting solutions are basic. The solution containing the tin ion is a strong reducing agent; the lead complex is used to remove sulfur from petroleum.

When a solution of stannic chloride ($SnCl_4$) is treated with ammonium hydroxide, a white colloidal gel of the metallic hydroxide is precipitated. As in the case of most metallic hydroxides, no definite formula can be assigned to it beyond regarding it as a hydrated oxide, $SnO_2 \cdot x\,H_2O$. Treated with strong acids, it forms salts, such as the sulfate, $Sn(SO_4)_2$; and treated with sodium hydroxide, it dissolves to form the sodium salt of an acid assigned the formula H_2SnO_3, called metastannic acid. A few salts are known derived from the acid H_4SnO_4, called orthostannic acid. The compound formed by the action of nitric acid on tin has approximately the formula of metastannic acid.

Sodium metastannate (Na_2SnO_3) is formed by adding an excess of sodium hydroxide to stannic hydroxide gel or by fusing stannic oxide with sodium carbonate:

$$SnO_2 + Na_2CO_3 \longrightarrow Na_2SnO_3 + CO_2\uparrow$$

It is used in making cotton cloth fireproof, in weighting silk, and as a mordant. The soluble stannate enters into the fibers of the fabric and is there precipitated by ammonium hydroxide or by steam.

Plumbic hydroxide, $Pb(OH)_4$, is not known, but plumbates derived from it can be obtained. Two of these are of interest. One is a red compound of the composition Pb_2O_3, but is really a plumbous salt of metaplumbic acid (H_2PbO_3), and its formula may be written $PbPbO_3$ or $PbO \cdot PbO_2$. The other is the pigment *red lead*, sometimes called *minium*, which is a plumbous salt of orthoplumbic acid (H_4PbO_4) and has the composition Pb_2PbO_4 or Pb_3O_4. When treated with nitric acid, two thirds of the lead in red lead is converted into lead nitrate, while the other third forms the dioxide:

$$Pb_2PbO_4 + 4\,HNO_3 \longrightarrow 2\,Pb(NO_3)_2 + PbO_2\downarrow + 2\,H_2O$$

As a pigment, red lead is especially effective in protecting structural steel from rust. Mixed with oil, it forms a paste used in making joints in gas pipes gastight.

The Sulfides of Tin and Lead · Apart from the native ore galenite (PbS), the sulfides of tin and lead are of interest chiefly in chemical analysis. From an acid solution of their salts, hydrogen sulfide precipitates *black lead sulfide* (PbS) from *all* simple lead salts; *brown* stannous sulfide (SnS) from stannous salts; and *yellow* stannic sulfide (SnS_2) from stannic salts. All these sulfides are insoluble in dilute acids, but the sulfides of

tin dissolve in yellow ammonium sulfide, $(NH_4)_2S_2$, to form *thiostannates*, while lead sulfide does not dissolve:

$$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_3$$
$$SnS_2 + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_3 + S$$

From these solutions stannic sulfide is precipitated by the addition of acids:

$$(NH_4)_2SnS_3 + 2\ HCl \longrightarrow 2\ NH_4Cl + H_2S\uparrow + SnS_2\downarrow$$

The slow precipitation of lead sulfide in alkaline solution forms a mirror-like deposit on the walls of the vessel; mirrors made in this way are widely used as rear-view mirrors in automobiles.

The Halogen Compounds of Tin and Lead · *Stannous chloride* is made by dissolving tin in hydrochloric acid, and crystallizes from solution as the hydrate $SnCl_2 \cdot 2\ H_2O$, often called *tin salt*. It is used as a mordant in the dye industry and also as a reducing agent. The stannous ion of all simple stannous compounds tends to pass into the tetravalent stannic ion, as illustrated in these equations:

$$SnCl_2 + 2\ HgCl_2 \longrightarrow SnCl_4 + Hg_2Cl_2$$
$$SnCl_2 + 2\ FeCl_3 \longrightarrow SnCl_4 + 2\ FeCl_2$$

Anhydrous stannic chloride ($SnCl_4$) is prepared industrially by treating tin scrap (or even used tin cans) with chlorine gas. It is a heavy colorless liquid which boils at 114° and freezes at −30°. In moist air it reacts vigorously with the water vapor and forms hydrogen chloride and dense clouds of stannic oxide. Stannic chloride dissolves in water, with strong heat evolution and with considerable contraction of volume. From such a solution a number of hydrates have been prepared, of which the pentahydrate, $SnCl_4 \cdot 5\ H_2O$, is the usual one.

From solutions of this salt in hydrochloric acid a compound called *chlorostannic acid* (H_2SnCl_6) can be isolated; the corresponding *fluostannic acid* (H_2SnF_6) is also well known. These yield long series of salts, of which ammonium chlorostannate, $(NH_4)_2SnCl_6$, called *pink salt*, is the most important. This salt, as well as stannic chloride, is used in weighting silk and cotton cloth and as a mordant. The compounds of tin with bromine or iodine require no special mention.

Lead chloride ($PbCl_2$) is a well-crystallized colorless salt, moderately soluble in hot water and nearly insoluble in cold water. It is precipitated from acid solutions when hydrochloric acid is added to a solution of a lead salt:

$$Pb(NO_3)_2 + 2\ HCl \longrightarrow 2\ HNO_3 + PbCl_2\downarrow$$

Lead tetrachloride ($PbCl_4$) is a very unstable heavy liquid that spontaneously loses chlorine, as does manganese tetrachloride (p. 686), and is reduced to ordinary lead chloride.

Other Compounds of Lead · Not many other compounds of tin have large uses in the arts and industries, but some lead compounds are of much importance and will be described briefly.

Tetraethyl lead ($Pb(C_2H_5)_4$). This is a covalent compound of tetravalent lead that has come into wide use as an "antiknock" in motor gasoline. A very little of it greatly improves the quality of a motor fuel for high-compression gasoline engines; but since it is a poisonous compound, gasoline containing it (ethyl gas) should not be used for household purposes. It is made by first making an alloy of sodium in lead of about the composition NaPb, and treating this alloy with ethyl bromide (C_2H_5Br) or ethyl chloride:

$$4\ C_2H_5Br + 4\ NaPb \longrightarrow Pb(C_2H_5)_4 + 4\ NaBr + 3\ Pb$$

Lead carbonates. Normal lead carbonate ($PbCO_3$) can be prepared as a white crystalline precipitate by treating a solution of a lead salt with sodium bicarbonate. A basic carbonate, $(PbCO_3)_2 \cdot Pb(OH)_2$, is of much more industrial importance than the normal salt because of its wide use in the manufacture of paints. In commerce it is called *white lead.* A large percentage of all the lead produced goes into the manufacture of white lead and other lead pigments.

Manufacture of white lead. The old and still standard way of making white lead is called the *Dutch process* because it was devised and first used in Holland in the seventeenth century. In this process metallic lead is cast in the form of plates and is exposed to carbon dioxide and the vapors of acetic acid.

The Dutch process is a very slow one, and more rapid ones have been devised that give very satisfactory products. One process depends upon electrolysis. The anode is a heavy lead plate dipping into a solution of sodium acetate and acetic acid; the cathode is an iron plate dipping into a solution of sodium carbonate; and the two solutions are prevented from mixing mechanically by a porous diaphragm. The lead ions, on their way to the cathode, meet the CO_3^{--} ions near the cathode and precipitate as the basic carbonate. The acetic acid set free attacks the lead anode.

In a second process very finely divided lead, together with dilute acetic acid, is slowly rotated in barrel-shaped cylinders in which a regulated pressure of carbon dioxide is maintained.

Lead Nitrate ($Pb(NO_3)_2$) · This salt is readily obtained by dissolving metallic lead or litharge in nitric acid. It crystallizes in octahedra and is easily soluble in water.

Lead Acetate ($Pb(C_2H_3O_2)_2$) · The acetate is obtained by dissolving litharge in concentrated acetic acid, from which it crystallizes in snow-white monoclinic

crystals of the composition $Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$. The alchemists called it *sugar of lead* because of its sweetish taste. The nitrate and acetate are the important *soluble* salts of lead.

Lead Sulfate ($PbSO_4$) · Lead sulfate is a white crystalline solid, insoluble in water and dilute acids. It is therefore formed as a precipitate whenever the ions Pb^{++} and SO_4^{--} are brought together in solution. Sublimed White Lead is a trade name given a white pigment made by heating galena (PbS) in a current of air to a suitable temperature. Its composition may be represented as a mixture of lead sulfate, lead oxide, and a little zinc oxide.

Lead Chromate ($PbCrO_4$) · This bright-yellow salt, called *chrome yellow*, results as a precipitate when solutions of a lead salt and a chromate are brought together:

$$Pb(C_2H_3O_2)_2 + K_2CrO_4 \longrightarrow PbCrO_4\downarrow + 2\ KC_2H_3O_2$$

By boiling the normal chromate with a solution of an alkali, a brick-red basic salt is obtained, called *chrome red*, which has the formula $PbCrO_4 \cdot PbO$. Both the *chrome yellow* and the *chrome red* are used as pigments.

Lead Arsenate ($Pb_3(AsO_4)_2$) · This compound is a white insoluble powder difficultly soluble in water, prepared by treating lead acetate with sodium arsenate. It is extensively employed as an insecticide.

QUESTIONS

1. (*a*) In terms of atomic structure, account for the fact that the hydroxides of carbon and silicon are acidic while those of tin and lead are amphoteric or basic. (*b*) Would you expect lead hydroxide to be a strong base? Explain. (*c*) In the light of your answer to *b*, would a solution of lead nitrate be basic, neutral, or acidic? Why?

2. Tin and lead were confused by the ancients. How could you tell samples of the two metals apart most easily?

3. Aside from that of tin, what other examples can you name of the transformation of an element or compound from one form into another at a definite transition temperature?

4. Suggest two methods for recovering tin from old tin cans.

5. Why is tin pipe, rather than lead pipe, used for carrying distilled water from one part of a laboratory to another?

6. (*a*) What compounds analogous to fluostannic acid have we studied? (*b*) What is the oxidation state of the central element in each case? (*c*) What other elements might be expected to form similar compounds?

7. What hydroxides of metals besides those of tin and lead are soluble in alkalies?

8. Why are white paint pigments other than white lead now so extensively used, particularly in manufacturing cities?

9. What are the differences in the reaction of nitric acid on tin and on lead?

10. What other elements give acids with formulas similar to the formula of stannic acid?

11. What is the reaction between the lead oxide, Pb_2O_3, and nitric acid?

PROBLEMS

1. How much lead peroxide can be obtained from 100 g of red lead by the action of nitric acid?

2. If we assume that metallic lead costs 10 cents a pound and white arsenic 6 cents, which of the two would be the more expensive material in the manufacture of lead arsenate?

3. One hundred grams of potassium fluostannate was transformed into the corresponding salt of fluozirconic acid. What did the product weigh?

4. A sample of cast iron weighing 1 g was dissolved in hydrochloric acid and oxidized to ferric chloride. This was reduced to ferrous chloride with a solution of stannous chloride, 1.6 g being required. What was the percentage of iron in the sample?

5. A sample of 1 g of white lead was dissolved in acetic acid, and 52 ml of carbon dioxide (standard conditions) was obtained. What was the percentage purity of the sample?

CHAPTER 45

THE CERAMIC INDUSTRIES

The Ceramic Industries · There are a number of industries based upon the use of clay, sand, limestone, and feldspar in varying degrees of purity; and, in so far as they involve chemical transformations, they are closely allied. To a greater or less extent they depend upon the formation of silicates at high temperatures from the materials named, the bases of which are chiefly oxides of sodium, potassium, calcium, magnesium, aluminum, and iron. These industries are often called collectively the *ceramic industries*. They include those industries engaged in manufacturing various products from nonmetallic, inorganic materials by processes that require high temperatures. They may be grouped roughly into three classes, according to whether they are most closely related to the manufacture of glass, cement, or clay products.

Glass

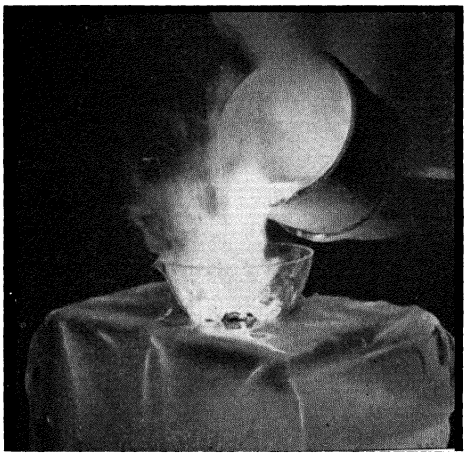
Nature of Glass · A glass is essentially a material which, on cooling from the state of a viscous liquid, has failed to crystallize and yet has become a rigid body; in other words, glass is an undercooled liquid. Pure silica, when fused and cooled, is an example of the simplest of glasses. The ordinary commercial varieties of glass are fused mixtures of silicates, together with excess of silica. When melted, these ingredients all mix to form a homogeneous liquid; and when this is cooled, it gradually stiffens and hardens to a glass. By the proper selection and proportioning of the ingredients a great variety of glasses can be made.

Varieties of Glass · Ordinary *window glass* is essentially a soda-lime-silica glass. The approximate composition is, in per cents, 72 SiO_2, 14 Na_2O, 13 CaO, and 1 $Al_2O_3 + Fe_2O_3$. Glass of this sort is perceptibly attacked by chemical reagents and even by water.

Flint glass contains a considerable addition of lead oxide. It is a "soft" glass; that is, it is easily softened by heating. It is very brilliant and has a high refractive index. Its composition, in per cents, is 40–50 SiO_2, 8–11 K_2O, 38–53 PbO, and 1 ($Al_2O_3 + Fe_2O_3$). Such a glass is suitable for some optical purposes and for the preparation of artificial diamonds and other imitation gems (*paste*).

Pyrex is essentially silica (SiO_2), softened by the addition of boric oxide (B_2O_3). The composition usually is, in per cents, about 80.5 SiO_2, 12.9 B_2O_3, 3.8 Na_2O, 0.4 K_2O, and 2.2 Al_2O_3. Pyrex is very resistant to chemical attack, and it withstands mechanical shock very well. Like silica, the ingredient present in largest amount, it expands and contracts only very slightly as the temperature goes up and down. Therefore it is a very satisfactory glass out of which to make chemical glassware, such as beakers and flasks; and it is used extensively in kitchenware of various sorts.

96-Per-Cent-Silica Glass · The higher the silica content of a glass, the higher its softening point and the less it expands and contracts when the temperature changes. It is difficult, however, to melt and fabricate glasses of higher silica content than Pyrex. It has been found that borosilicate glasses containing about 75 per cent silica can be melted and molded in the usual way, then given a heat treatment which causes the alkali borates to separate from most of the other constituents. Treatment of the molded glass article with dilute acid then leaches out the alkali borates, leaving a porous skeleton containing 96 per cent silica. When washed and dried at 1200° C, this skeleton shrinks to 65 per cent of its original volume without change in shape, and the glass becomes transparent. The resulting glass is known as Vycor.



Corning Glass Works

Fig. 45-1. High-Silica Glass Molten metal being poured into a Vycor dish which rests on a cake of ice. This glass can be subjected to temperatures up to about 1000° C without melting or cracking

Color of Glass · The color of glass is usually due to the presence of metallic color groups, probably ions. For example, ferrous ions color glass green, while ferric ions color it yellow or brown. The green color can be changed to the less objectionable yellowish tint by the addition of manganese dioxide, which acts as an oxidizing agent, converting the ferrous into ferric compounds. In larger quantities manganese colors glass violet. Cobalt compounds give a deep-blue color, and many other metals produce characteristic colors. Sometimes the metals themselves are added and form a colloidal dispersion. Copper and gold are added to

glass to produce a rich ruby-red color. Selenium also gives a beautiful red color to glass and is used both to produce this color and (in smaller percentages) to compensate for the green of ferrous color groups. Opaque, or milky, glasses are made by dispersing fine crystalline material in the hot melt; these particles remain suspended when the glass is cooled, and make it turbid. Fluorite, cryolite, calcium phosphate, and tin oxide are the most common materials added to produce that effect.

Special Glasses · It should be kept in mind that the applications of glass in the arts and industries are increasing all the time. Each new application is apt to present a new problem, to be solved by modifying the composition of the glass, or by manipulating it during manufacture, so as to give it properties exactly suited to the new use. Many such problems have been solved, but some still await solution.

Optical glass. Until the early part of the present century, Germany supplied the United States with the special glass used in making lenses for microscopes, cameras, field glasses, and other optical instruments. During the war of the second decade it was necessary to develop production in this country and with the utmost speed. It was not difficult to learn the exact composition of optical glass by analysis. The trouble lay partly in the difficulty of securing pure materials, not only for the glass itself but also in the construction of the glass-pots in which the glassmaking is carried out, and partly in discovering the proper mechanical methods for carrying on the operation. For, if any iron is present in the materials, the resulting glass has some color, while if the operation is not carried on in the right way, the glass is not homogeneous; and either of these defects is fatal for optical glass. The problem was solved successfully, and the United States now produces optical glass in excess of its needs.

Glass transparent to ultraviolet light. Glass is transparent to light, but it absorbs most of the waves beyond the visible violet of the spectrum, called *ultraviolet light.* These waves have the greatest chemical and germicidal value, and the sunlight that comes to us through glass windows has but a small part of the value of direct sunshine. Pure silica glass transmits this ultraviolet light, but it is very expensive and can be made in small pieces only. Much progress has been made in the production of a cheap glass that transmits ultraviolet light, and transparent plastics have been developed that accomplish the same purpose.

Window glass. Until recent times window glass was made by blowing plastic glass into long cylinders which were cracked lengthwise, heated until soft, and then flattened into sheets in much the same way as a cylindrical tube of paper, when cut lengthwise, will open to form a

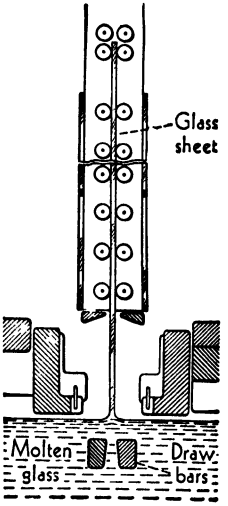
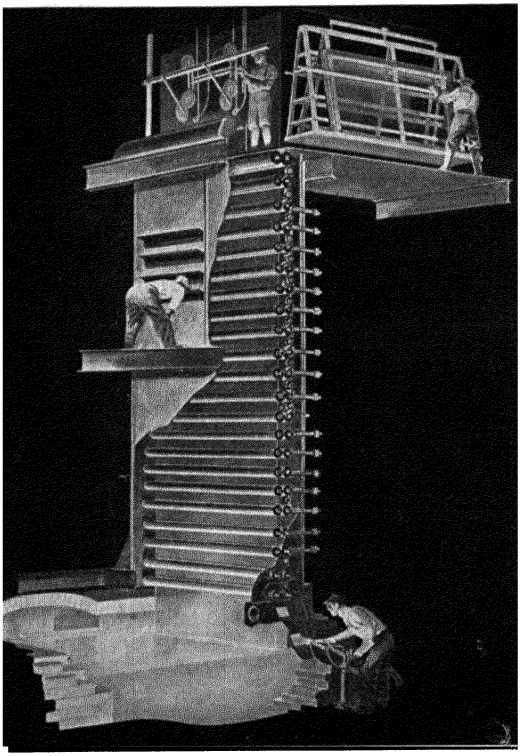


Fig. 45-2. Drawing Sheets of Glass from Molten Glass

flat surface. This method has given way to other devices by which liquid glass is worked directly into continuous sheets, which are then cut into desired sizes. Several methods are used for doing this, but the principal one is the following:



Pittsburgh Plate Glass Co

Fig. 45-3. The Manufacture of Window Glass A set of rolls draws the glass upward vertically after it has been introduced by a bait

The raw materials are put into a large furnace lined with refractory brick, and then heated with producer gas (or some other gaseous fuel or liquid fuel, such as oil) until the reaction is complete and the glass is in the form of a viscous liquid. To start the operation, a thin steel band (called the bait) is lowered into the glass and slowly withdrawn. The viscous glass adhering to the bait draws a continuous sheet of thick plastic glass upward between rollers, as shown in Fig. 45-2. As the sheet advances (25 ft or more), it cools, and emerges from the top rollers as a solid sheet, which can be cut into the desired sizes (Fig. 45-3).

When once started, the operation continues during the life of the furnace (ten months or more). Raw materials are fed into one end of the furnace, and the melted glass is removed from the other end. Enormous quantities of window glass are manufactured yearly.

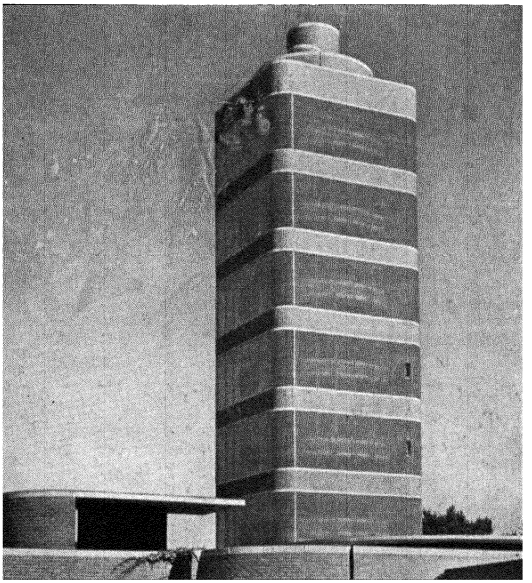
Plate glass. This form of glass is too thick to be made like ordinary window glass. A common method of making it consists in feeding plastic glass between a set of rollers, from which it emerges horizontally onto a smooth surface. When cooled, it is polished, first with fine sand, and then with an oxide of iron known as "rouge."

Shatterless (safety) glass. This kind of glass, now largely used in automobiles, owes its chief property to its construction rather than to its composition. It is prepared by putting a sheet of some plastic between two plates of glass and heating the combination under pressure.

Glass bricks. These are coming into use as a building material. The bricks are hollow, and are made by cementing together two half-bricks. Houses built of them require no windows, as the brick walls are fashioned so as to admit the

proper amount of diffused light. They are especially adapted for building houses that are air-conditioned.

Glass fibers. One of the most important developments in glassmaking is that of fashioning glass in the form of wispy filaments, a few ten-thousandths of an inch in diameter, so small that a large number of them are required to form a fiber no larger than an ordinary thread. The tensile strength of these fibers is comparable to that of steel. They are now produced in two forms: (1) "staple" fiber, averaging about 9 in long- used for heat insulation, for electrical insulation, and as a dust filter; (2) continuous filament, used in making woven fabrics. The manufacturers of this material state that "the length of insulating wool fibers produced in one hour on one glass machine is more than 100 times the distance around the earth at the equator."



Corning Glass Works

Fig. 45-4. Glass Building · More than 20 miles of Pyrex tubing were used to make the walls of this 15-story structure. Between brick bands, the tubing has been literally wound around the tower from top to bottom. These window-walls have the strength and insulating qualities of masonry, and are excellent light transmitters.

Invisible glass. At least 8 per cent of the light that strikes the ordinary window glass is reflected from its two surfaces. It is because of this fact that the glass in our windows is visible. Recent experiments have shown that glass becomes invisible when coated with an exceedingly thin film of certain materials, such as sodium and magnesium fluorides or a particular kind of soap. To produce this effect, the films must have just the right thickness so that the reflected wave of light will be exactly neutralized by the oncoming waves. Glass lenses for use in fine optical instruments are commonly treated in this way, in order to reduce the reflective losses which otherwise occur at the many surfaces in a multilens system.

Molding and blowing of glass. The way in which the melted mixture is handled in the glass factory depends upon the character of the article to be made. Some articles, such as ornaments and complicated chemical glassware, are mouth-blown directly into the finished product (Fig. 45-5). This requires great skill that can only be attained by years of practice. Many other articles, such as bottles, are made by blowing the plastic glass, either by the mouth or by compressed air, into hollow molds of the desired shape. The mold is first opened, as



Corning Glass Works

Fig. 45-5. Glass-blower Making a Condenser

shown in Fig. 45-6 A lump of plastic glass, *A*, on the hollow rod, *B*, is lowered into the mold, which is then closed by the handles, *C*. By blowing into the tube the glass is expanded into the shape of the mold. The mold is then opened and the object lifted out. The neck of the object must be cut off at the proper place and the sharp edges rounded off in a flame. Bottles are now made chiefly by machines that produce the finished product entirely by mechanical means. The first of these machines was devised by Michael J. Owens in 1899, but it was a rather crude device. Continued improvements have now brought these machines to such a high state of perfection that a single machine will turn out 100,000 bottles daily.

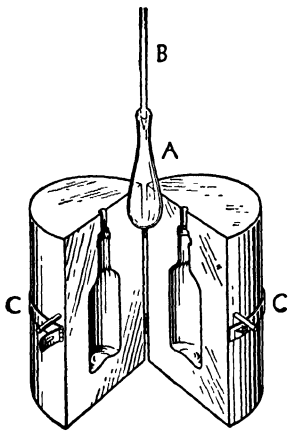


Fig. 45-6. Making a Glass Vessel in a Mold

Other objects, such as lamp chimneys, tumblers, and beakers, are also made by molding. The glass is revolved while being blown into the mold so as to avoid the formation of a ridge where the mold closes. Electric-light bulbs, originally mouth-blown,

are now produced by machines brought to such a state of perfection that two machines will turn out more than 1,000,000 bulbs daily.

Annealing of glass. Melted glass, when cooled quickly, becomes very brittle. For this reason, glass articles, always hot when first fashioned, are cooled slowly, generally by passing them through a long furnace the temperature of which gradually diminishes from one end to the other.

Tempered glass. If the surface of a glass plate is heated nearly to the softening point and then cooled quickly in a blast of cold air, the glass becomes much more resistant to shock than glass as ordinarily annealed. Such tempered glass is used industrially where glass must be subjected to compression, and finds some application in domestic utensils, such as "unbreakable" tumblers.

Cement

Properties of Cements · The term *cement* is usually applied to a silicate material which, mixed with water, forms a paste that becomes hard and durable on standing. These properties make it a useful material for many purposes, especially for joining bricks and stones and for building construction in general. Mixed with sand and crushed stone, it forms *concrete*, largely used in the foundations of buildings, road construction, dams (Fig. 45-7), and similar structures. Where great strength is required, iron rods or wire is embedded in the concrete before it sets, and this is known as *reinforced concrete.*

There are many different kinds of cements, but the most important and the most largely used is Portland cement. This has the additional advantage of hardening under water.

Portland Cement · The material called Portland cement has long been known. The Romans used a similar cement at an early date, for building water conduits and as foundations for buildings and other structures. Its durability is shown by the fact that many of these conduits and foundations still exist in fairly good condition. The first real Portland cement was made in England in 1824 and was named because of its resemblance to a natural rock found on the Isle of Portland. Portland cement was first made in the United States in 1872, when a plant was built in the Lehigh valley, Pennsylvania. The industry, slow in development, gradually advanced until, in 1952, the production amounted to 250,000,000 barrels—an amount far greater than that produced in any other country.

Manufacture of Portland Cement · The chief materials employed in the manufacture of Portland cement are limestone, clay, shale, blast-furnace slag, marl, iron ore, and gypsum. The materials are coarsely ground, then mixed together in the proper proportions with water and finely pulverized. The resulting mixture, or slurry, is run into a rotary

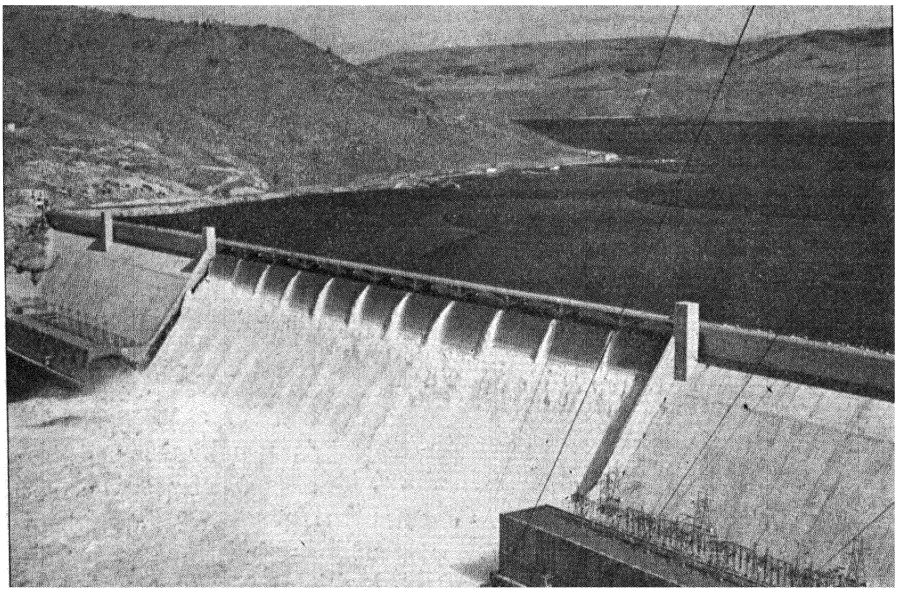


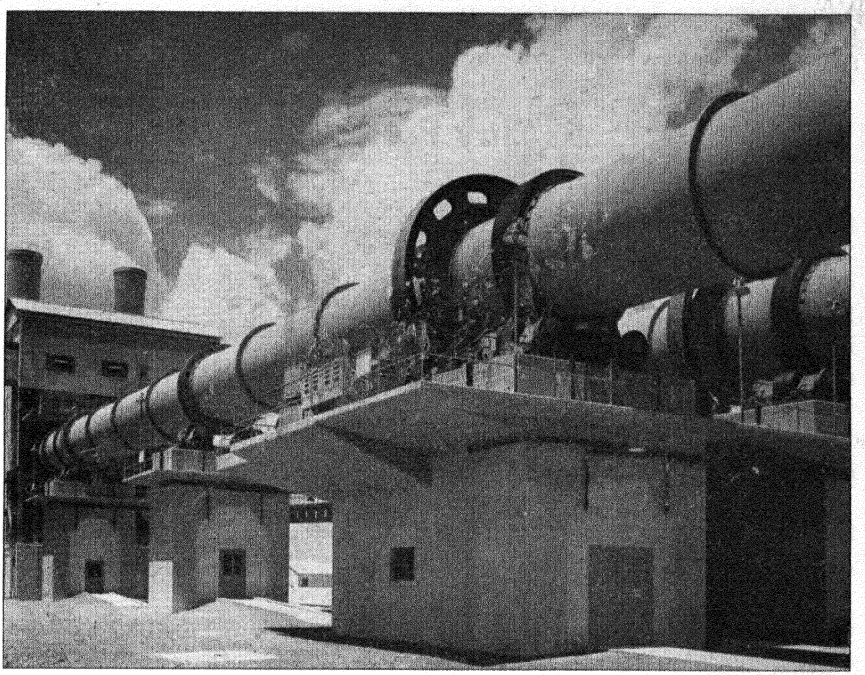
Fig. 45-7. Grand Coulee Dam This dam is the largest concrete structure in the world. It contains about 10 million cubic yards of concrete, and weighs about 22 million tons. The same amount of concrete would build a modern highway 4300 miles long.

kiln (Fig. 45-8) after dewatering, and heated to a temperature just short of fusion, at which temperature it vitrifies and forms a grayish mass called *clinker*. The process of silicate formation is not so complete as in the case of glass, but definite compounds are formed. Finally the clinker is ground and mixed with a definite percentage of gypsum, which regulates the rate of setting of the cement when mixed with water.

The Composition and Setting of Portland Cement · The composition of a material made of so many natural products varies rather widely but must be kept within certain limits. The chief compounds present in Portland cement, together with the time of setting of each, are as follows:

COMPONENTS OF PORTLAND CEMENT AND TIME OF SETTING	COMPOUNDS	TIME OF SETTING
	Dicalcium silicate ($2\,CaO \cdot SiO_2$)	28 days
	Tricalcium silicate ($3\,CaO \cdot SiO_2$) . . .	7 days
	A mixture of the following aluminates: $3\,CaO \cdot Al_2O_3$ and $4\,CaO \cdot Al_2O_3 \cdot Fe_2O_3$	1 day

The reactions which take place in the setting of cement are not entirely understood. Apparently the compounds present undergo hydrolysis in contact with water, and the resulting compounds unite with water to



Portland Cement Association

Fig. 45-8. View of Twin Rotary Kilns Used in Making Cement · Each tube is 12 feet in diameter and as long as a 40-story building. It slopes downward from the far end, where raw materials are fed in. As the materials move slowly along the rotating tube, they are subjected to increasing temperatures that finally reach 1500° C, produced by burning finely powdered coal, fuel oil, or gas at the lower end of the tube. The clinker thus formed is later ground to make cement

form hydrates, which produce the hard compact mass. The process of setting takes place best in air; but when the process is wholly or partially completed, the mass may be placed under water, since the compounds present are all insoluble.

Other kinds of cement. The quick-setting cements rather widely used are made by heating a mixture of bauxite and limestone and grinding the resulting mass to a fine powder. They consist of complex calcium aluminates, which set more quickly than Portland cement (see the table on page 768). They are not as permanent as Portland cement but serve when quick setting is important. Another quick-setting cement is composed of tricalcium silicate, which sets in seven days, as contrasted with the twenty-eight days required for the average Portland cement.

The so-called *oxychloride cements* are composed largely of the compound $3\ MgO \cdot MgCl_2 \cdot 10\ H_2O$. They differ from Portland cement in that they are elastic and are especially adapted for making floors. An admixture of powdered

metallic copper improves these cements. There are many varieties of dental cement. A common kind is made by mixing zinc oxide with phosphoric acid.

Clay Products

Brick and Draintile · The crudest forms of clay products, such as porous brick and draintile, have little chemistry involved in their manufacture. The clay is molded into the required form, dried, and then fired in a kiln, but not to a temperature at which the materials soften. In this process the nearly colorless ferrous compounds in the clay are converted into ferric compounds, which give the usual red color to these articles. In making vitrified brick the temperature is raised to the point at which fusion begins, so that the brick is partially changed to a kind of glass. Insulators for electrical wiring and spark plugs are special types of ceramic products.

White Pottery · This term is applied to a variety of articles, ranging from the crudest porcelain to the finest chinaware. While the processes used in the manufacture of the articles differ in details, fundamentally they are the same and may be described under three heads: (1) the preparation of the body of the ware, (2) the process of glazing, and (3) the decoration.

1. **The body of the ware.** The materials used consist of an artificially compounded body made from kaolin, plastic clay, pulverized quartz (known as Potter's flint), and pulverized feldspar. This mixture is plastic and is worked into the desired shape by molds or on a potter's wheel. The ware is then dried and fired to the desired density, and in this form is known as *bisque*. This is usually porous and must be glazed to render it nonabsorbent. Some whiteware is fired to a nonporous condition and glazed at the same time.

2. **The glaze.** The glaze is a fusible glass which is melted over the surface of the body. The constituents of the glaze are quartz, feldspar, limestone, clay, and various metallic oxides, often mixed with a little boric oxide. These materials are finely ground, or sometimes fused into a glass and ground, and then mixed with water to give a slip, or slurry. The bisque is dipped into this glaze slip and then fired (Fig. 45-9) until the materials composing the glaze fuse and produce a smooth, glossy surface. The glaze must be so chosen as to resist the reagents to which it is to be exposed, and it must have the same coefficient of expansion as the body; otherwise it will check, or crackle, when the vessel is exposed to changes of temperature. It is evident that the calculation of a glaze for a given body requires a very thorough knowledge of the physical constants of the materials from which the body was made, as well as of the properties contributed to the glaze by each ingredient.

3. **The decoration.** If the article is to be decorated, the design may either be painted upon the body before glazing, when it is said to be underglazed, or be



Fig 45-9. The Manufacture of Porcelain Plates and Similar Wares The picture shows the burning of the wares in a kiln. Various kinds of kilns are used, the one shown is circular in shape The wares are placed on shelves that slowly revolve through a highly heated kiln

painted upon the glaze and the article fired again, so that the pigments melt into the glaze. In the latter case it is said to be overglazed. In the former case the pigments used are, as a rule, metallic oxides, while in the latter case they are often colored glasses.

Enamels · Enamels are glazes applied to surfaces of various kinds, chiefly metals, to produce a smooth, vitreous, opaque surface which protects the body of the ware from rust Graniteware cooking utensils, and plumbing accessories (such as bathtubs), are familiar illustrations The enamel must be designed to correspond to the coefficient of expansion of the metal to which it is applied through the range of temperature to which it will be exposed; otherwise it will crack. It must also adhere firmly to the surface

Tableware Made from Synthetic Resins (Plastics) · Attention has been called to the many uses of plastics. They are especially adapted for making certain grades of tableware, for they are not easily broken and may be readily decorated and colored. But they will not withstand much heating.

Refractories · Materials that are resistant to the action of heat—capable of enduring high temperatures without softening—are called *refractories*. They are used for making crucibles and for lining furnaces where high temperatures must be withstood. Refractories are acid (as silica and fire clay), basic (as magnesite and dolomite), or neutral (as chromite and graphite). The type of refractory to be employed in a particular case is selected so that chemical reaction with the charge with which it is to be in contact will be prevented as far as possible. Thus the life of the furnace is prolonged.

Refractories are used, for example, for the construction or lining of blast furnaces (p. 611), open-hearth furnaces (p. 615), Bessemer converters (p. 614), glass melting-pots (p. 764), kilns for the production of ceramic ware (Fig. 45-9), rotary kilns for the manufacture of cement (p. 769), boiler furnaces of the power industry, and even household furnaces. Because the successful operation of so many of the industrial processes that are vital to our way of life is dependent, directly or indirectly, upon the availability of satisfactory refractories, a great deal of research effort is being constantly devoted to the development of new and more effective refractory materials.

QUESTIONS

1. What is the difference between kaolin and clay?

2. Why does glass sometimes have bubbles in it?

3. Is the glass of an automobile windshield really "nonshatterable"?

4. (*a*) Why not use sodium phosphate in making glass rather than sodium sulfate? (*b*) Why not sodium chloride? (*c*) Why not sodium nitrate?

5. What are the reactions that take place when glass is made from sodium sulfate, carbon, and sand?

6. Does the statement that ordinary window glass "approximates the formula $Na_2O \cdot CaO \cdot 6\,SiO_2$" imply that glass is an impure compound?

7. If water should act upon ordinary window glass, what reactions should you expect to take place?

8. Why will ordinary mortar not set under water?

9. What are some of the properties that must be possessed by the porcelain that surrounds the wire of an automobile spark plug?

10. Why are telegraph wires strung on glass supports, while high-tension wires are carried on porcelain? Why not use porcelain supports for both?

11. What is the probability that plastics will replace pottery? Give reasons for your answer.

PROBLEMS

1. To make glass of the composition corresponding to the formula $Na_2O \cdot CaO \cdot 6\,SiO_2$, in what proportion must the following ingredients be brought together: sodium sulfate, calcium carbonate, sand?

2. Suppose that you desire to make 1 kg of a hard glass of the Pyrex type and of the following composition: SiO_2, 80 per cent; B_2O_3, 12 per cent; Al_2O_3, 3 per cent; Na_2O, 5 per cent. Suppose that the available materials are SiO_2, B_2O_3, $Al_2Si_2O_7$, and $Na_2B_4O_7$. What weight of each will be required?

CHAPTER 46

THE CHEMISTRY OF THE SOIL; FERTILIZERS; INSECTICIDES AND FUNGICIDES; PURIFICATION OF WATER

Introduction · The natural interest which a chemist has in the composition of the earth takes various forms. He has an intellectual curiosity about the composition of the earth as a whole. He poses such questions as "Is the earth alike all the way through, or is it different in the interior, and how would one proceed to find out?" "Is the composition of the earth as a whole like that of the other planets and the sun?"

He has a very practical interest in the earth's crust, at least in that part of it which he can reach by digging holes or boring wells. From this part of the earth are obtained many of the mineral materials which are used in our way of life. Such things as iron ore, sulfur, petroleum, copper, lead, marble, calcium phosphate, and coal are taken from the earth's crust.

He has a vital interest in the thin layer on the earth's surface which we call the *soil*, because much of life depends on this layer and on the chemical and biological changes which take place in it or because of it.

The Composition of the Earth's Core · It is easy to calculate the total volume occupied by the earth-sphere. The radius of the earth is about 6.37×10^8 cm; its volume ($\frac{4}{3}\pi r^3$) is about 1.083×10^{27} ml. The total mass of the earth can be calculated from the magnitude of the force of gravity, and the best figure for it is 5.98×10^{27} g. The average density is, therefore, $\frac{5.98 \times 10^{27}}{1.083 \times 10^{27}} = 5.52$.

But the density of the rocks in the earth's crust is about 2.8, and consequently we must infer that the earth's interior is made up of materials much more dense than those in the crust. Much of our inference about the internal structure is based on a study of the velocity of earthquake waves which reach the various seismograph stations located around the earth. A wave may start, say, at a point A (in Fig. 46-1) and travel through the crust and also through the interior at different depths to points B, C, and D. Since the velocity depends on the density of the medium through which the waves travel, we have here the basis for an

estimate of density at various depths. A current theory of the nature of the earth's interior is illustrated in Fig. 46-1. A central core about 3400 km (1800 miles) in radius is thought to be made up of iron (and nickel) and to have a density of approximately 10. Whether it is liquid or solid is not known. Around this core there is a transition layer, of the thickness shown in the figure, and then there is a magnesium-iron silicate layer of density approximately 4. On top of all is the crust (lithosphere) of the earth, 60–100 km deep (36 60 miles).

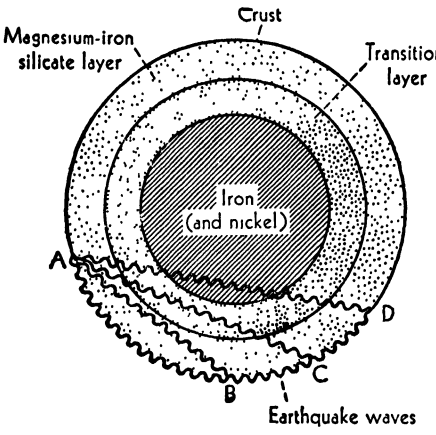


Fig. 46-1. Diagram of Supposed Composition of the Earth

The fact that meteors are composed of mixtures of iron and nickel suggests that the earth, too, which may have had the same origin, is made up in large part of iron and nickel.

Abundance of Elements in the Earth's Crust · Man has not yet been able to drill wells or dig mines much deeper than $4\frac{1}{4}$ miles; but geologists have obtained a good idea, from the faulting and uplifting of strata and enormous masses of rock, of what the crust is like down to depths of perhaps 10 miles. Systematic sampling and chemical analysis have been made for many years in the effort to learn the distribution and abundance of the various elements. The following table shows the average composition of the 10-mile-deep earth's crust in terms of the most commonly found elements:

	ELEMENT	PER CENT	ELEMENT	PER CENT
ELEMENTS IN THE EARTH'S CRUST (EXCLUSIVE OF THE OCEANS AND ATMOSPHERE)	Oxygen	46.71	Magnesium	2.08
	Silicon	27.69	Titanium	0.62
	Aluminum	8.07	Hydrogen	0.14
	Iron	5.05	Phosphorus	0.13
	Calcium	3.65	Carbon	0.094
	Sodium	2.75	Other elements	0.436
	Potassium	2.58		100.000

Oxygen constitutes almost half of the total; silicon more than a quarter; the first five elements, oxygen, silicon, aluminum, iron, and calcium, more than 91 per cent; and the twelve elements listed above, more than 99.5 per cent. Some of the other elements are extremely rare and difficult to find.

What May Have Happened When the Earth Cooled · Let us suppose that all the earth was at one time a hot glowing mass of vapor which gradually cooled, by radiation of its heat, and condensed to liquid and finally largely to solid. As the mass cooled to sufficiently low temperatures, oxides were formed. It is likely that iron made up a very considerable portion of the original mass, but that the oxides of iron (and nickel) were not formed until relatively low temperatures were reached, late in the process of cooling. In the meantime the vast masses of metallic iron (and nickel), being very dense, were largely segregated at the center. The much lighter oxides collected in regions outside this core, and the lightest ones at the very top. Finally, at still lower temperatures, oxides combined chemically with other oxides to give complex oxides, such as have been described in the chapter on the compounds of silicon. The formulas of four of these minerals are shown below.

NAMES AND FORMULAS OF SEVERAL MINERALS CONTAINING SILICON DIOXIDE

MINERAL	FORMULA	FORMULA AS A COMPLEX OXIDE
Wollastonite .	$CaSiO_3$	$CaO \cdot SiO_2$
Leucite . . .	$KAlSi_2O_6$	$K_2O \cdot Al_2O_3 \cdot 4\,SiO_2$
Albite	$NaAlSi_3O_8$	$Na_2O \cdot Al_2O_3 \cdot 6\,SiO_2$
Quartz . . .	SiO_2	

These rock minerals and others like them, as well as sedimentary materials derived from them, such as limestone, sandstone, clay, and shale, form the earth's crust.

The Soil · On the surface of the earth's crust is a relatively thin layer composed of a loose agglomeration of small rock particles, clay, and decayed vegetation, much of which is of colloidal size and which holds, mechanically or by adsorption, varying amounts of air, water, salts of various sorts, and other compounds. In it, too, are found living organisms of many kinds. This layer varies in thickness from that of the thinnest covering on practically bare rock to 30 ft or 40 ft in the valleys of the Nile and Mississippi. The average depth, however, is 6 in. to 12 in. The importance of this relatively thin layer over the earth cannot be overestimated because in it take place many of the chemical reactions involved in the growth of plants, and from it the plants draw the substances necessary for their growth (with the exception of oxygen and carbon dioxide from the air).

Uses of the Soil · Ordinarily we think of the soil as useful because it makes possible the growth of all the plants and trees that directly or indirectly provide our food. With more careful thinking we realize at once that plants and trees are the source of many valuable products other than

foods. We obtain rubber from rubber trees; drugs, such as quinine, from cinchona bark; and morphine from poppy pods. We also obtain from plants and trees fibers such as cotton and linen for clothing; wood for our homes; oils and resins for paints. Various substances from plants and trees are often the source materials for making hundreds of useful articles; for example, many useful resins and plastics are made from sap or seeds, and so many automobile parts are made from these plastics that one enthusiastic engineer has said (speaking figuratively, of course) that the time may come when we shall "grow" automobiles.

The percentage of farm products used for purposes other than for food is steadily increasing. Realizing that we have merely made a beginning in this direction the Federal government has established a number of research laboratories in which trained scientists are seeking new uses for farm products. "Chemurgic products" is a name coined to designate the industrial uses for farm crops; and it may be that some of the serious problems confronting the farmer may be solved by finding new uses for the things he can grow.

Formation of the Topsoil · The *inorganic constituents* of the soil have resulted from the agelong action of rain, ice, wind, and atmospheric gases on the surface rocks of the earth, a process called *weathering. Physically,* the rocks may be broken and crumbled by the expansion of water when it freezes. They may be worn away by the action of dust. *Chemically,* the action of water and of carbon dioxide has led to the disintegration of great quantities of the complex silicate rocks, like the granites; and the action continues at the present time.

Granite may be mentioned as a typical illustration of a *mixture,* since a granite may consist of (1) quartz and (2) some mica-like substance, embedded in (3) a matrix of feldspar. Let us take anorthite ($CaAl_2Si_6O_{16}$, or $CaO \cdot Al_2O_3 \cdot 6\,SiO_2$) as an example of a feldspar, and indicate what the chemical reactions may have been when it was attacked by water and carbon dioxide in the weathering process. The carbon dioxide attacked anorthite chemically and took out the lime (CaO) to form calcium carbonate ($CaCO_3$). What was left of the anorthite reacted with water to form kaolin, which is the chief constituent of common clay.

$$\underset{\text{anorthite}}{CaO \cdot Al_2O_3 \cdot 6\,SiO_2} + CO_2 + 2\,H_2O \longrightarrow \underset{\text{limestone}}{CaCO_3} + \underset{\text{kaolin}}{Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O} + \underset{\text{sand}}{4\,SiO_2}$$

Our enormously extensive deposits of clay and limestone probably originated in some such fashion.

When the feldspar of a granite had been attacked, or weathered, as

just described, the other two crystalline materials, the micalike substance and the quartz, were released mechanically from the conglomerate. After much physical pounding and battering the larger pieces of quartz were ground to sand. Most soils contain both clay and sand. Vast quantities of sand grains were matted together with mineral binding materials of various sorts, and beds of sandstone were thus laid down.

Further, the ions of calcium, as well as of magnesium, sodium, potassium, etc., were liberated from the insoluble crystals of the various types of feldspars in the chemical disintegration processes, with the formation of more soluble compounds. These compounds, present in the soil, and in ground waters, are used by growing plants.

The *organic constituents* of the soil result from the partial decomposition of organic matter, both plant and animal, which in turn results from the action of bacteria or molds (yeasts) on the dead plant and animal tissues. An important intermediate stage in this decomposition is *humus*, a colloidal, hygroscopic mixture of organic substances, somewhat acid in character, which exerts a profound influence on plant growth, largely because of its ability to absorb and hold water, up to five times its own weight. Soil containing humus holds water for long periods of time, whereas soil without humus tends to dry out rapidly.

Conservation of the Soil · From the relative thinness of the soil layer it is evident that it is produced only very slowly. It is, therefore, of great importance that it be preserved and that its fertility be maintained.

The enormous economic losses due to the erosion by wind and water which has resulted from the removal of forests and prairie grasses are the problem of the engineer and the conservationist. The removal of good topsoil observable in the muddy water of the Mississippi and Missouri rivers—in fact, in practically all rivers—and in the dust storms of the Southwest represents a dangerous loss of the nation's resources.

Of more direct interest to the chemist are the losses of the mineral constituents of the soil which are necessary to plant life. These constituents must be in soluble form in order to be useful. Hence they can be and are constantly leached out of the soil by rain. This process is slowed up when the colloidal condition of the soil is such as to favor the adsorption and retention of ions by soil particles, and when the humus content of the soil is high enough to prevent rapid loss of water.

Constant and repeated growing of the same crop, year after year, has a tendency to deplete the soil of one or more of its essential plant foods. Thirty bushels of wheat, for example, remove from the soil about 34 lb of nitrogen, 6.2 lb of phosphorus, 7.7 lb of potassium, and smaller amounts of sulfur, calcium, and magnesium; potatoes remove a relatively higher

percentage of potassium and less of nitrogen. The system of rotation of crops has been practiced by good farmers in many parts of the country to offset this depletion. The use of natural manures and the plowing under of cover crops such as clover, which can introduce nitrogen into the soil (p. 410), are other methods adopted by good farmers for maintaining soil fertility. However, agriculture is, to an ever-increasing extent, making use of commercial fertilizers to supply the minerals which plant life needs.

Fertilizers

The Necessity for Fertilizers · With the exception of carbon dioxide and oxygen absorbed from the air (and, of course, some water), the growing plant gets its nutriment from the soil. In order that vegetation may thrive it is essential, therefore, for the soil to contain an adequate supply of suitable plant food. The natural supply is continually being drawn upon by growing plants; and for the soil to retain its fertility the ingredients so withdrawn must be returned to it and in a form that can be assimilated by the plants. It is to supply this need that fertilizers are used (Fig. 46-2).

Constituents of Fertilizers · While a number of elements are essential to the growth of plants, experience has shown that in general the fertility of the soil may be maintained by the addition of four substances: (1) nitrogenous matter, (2) phosphates, (3) compounds of potassium, and (4) compounds of sulfur. It should be added, however, that our knowledge of what substances are essential to plant growth is far from complete. Recent experiments indicate that in addition to the elements long regarded as the only essential ones (carbon, oxygen, hydrogen, nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, and iron), small percentages of the following are also necessary for the growth of plants: copper, zinc, manganese, boron, and molybdenum (and for animals, cobalt and iodine in addition). The required amounts of these are very small, and it is probable that most soils have the necessary supply; if not, they must be provided and in a form that the plant can use. It should be noted that man and the animals need these elements in their food, and must get them ultimately from the plants which they eat. This subject is an interesting and important one for investigation, and the experiment stations of the national government and of the various states spend large sums of money annually in experimenting on the effects of fertilizers. In recent years extensive experiments on fertilizers have been carried on by the national government.



Courtesy of Mr Ballow, Newark, Ohio

Fig. 46-2. View of an Ohio Apple Orchard, Showing the Effect of Fertilizers The row of twelve trees on the left, fertilized with sodium nitrate and calcium acid phosphate, produced thirty barrels of apples The unfertilized row of twelve trees on the right produced only three barrels

Sources of Fertilizers · The industrial sources of each of the constituents of fertilizers are as follows:

1. **Nitrogenous matter.** This is obtained from a number of sources: sodium nitrate, ammonium sulfate, ammonium phosphate, cyanamide, urea and ammonia itself; also from nitrogenous organic matter, such as dried blood, the waste from slaughterhouses, and animal manures Formerly we secured all our sodium nitrate from Chile (p. 296) and ammonium sulfate from by-product ammonia in coal distillation (p. 396). At present a large percentage of these compounds is made from synthetic ammonia prepared by the Haber process.

2. **Phosphates.** Ground bones are especially valuable, since they contain some nitrogen in addition to calcium phosphate. This source is entirely inadequate, and the great supply comes from rock phosphates, which contain about 70 per cent of calcium phosphate. These rock phosphates are quarried in large tonnages, especially in Florida and Tennessee, and low-quality material can be concentrated by flotation. Since calcium phosphate is practically insoluble, it must undergo chemical treatment to make it available as a plant food. It is ground and treated

with sulfuric acid, which converts the insoluble phosphate into a soluble calcium hydrogen phosphate:

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\ CaSO_4$$

The resulting mixture of calcium hydrogen phosphate and calcium sulfate is a powder known commercially as *superphosphate of lime.* Since phosphoric acid is now produced cheaply by the oxidation of phosphorus, phosphate rock is sometimes treated with this acid rather than with sulfuric acid:

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \longrightarrow 3\ Ca(H_2PO_4)_2$$

A very concentrated fertilizer is thus produced, which saves transportation costs. Slags from the production of steel from ores containing phosphorus are sometimes used in making fertilizers.

3. **Potassium compounds.** The potassium for all industrial uses comes from salt deposits of potassium compounds, chiefly KCl (sylvite), $KCl \cdot MgCl_2 \cdot 6\ H_2O$ (carnallite), and $MgSO_4 \cdot K_2SO_4 \cdot 2\ CaSO_4 \cdot 2\ H_2O$ (polyhalite). For many years the agricultural world was dependent on the salt beds of Stassfurt (Germany) and of Alsace (France) for its fertilizer potassium. Similar but less extensive beds have been discovered more recently in a number of countries—for example, in the United States, in New Mexico (Carlsbad) and Texas. Potassium chloride is also extracted from Searles Lake, California, and to a lesser extent from brines, sea water, and certain mineral rocks. We still import thousands of tons of potassium salts from Europe.

4. **Sulfur compounds.** Reference to paragraph 2 (p. 779) will show that ordinary superphosphate of lime contains calcium sulfate, and this sulfur compound is beneficial to most soils. For growing certain crops, ground gypsum is sometimes added as a fertilizer.

5. **Plant-growth substances.** In addition to the fertilizing agents already described, it has been found that minute quantities of certain complex organic chemicals enormously stimulate plant growth, especially root growth (p. 570). These seem to act much as the vitamins of food or the hormones of the glands of the animal body. These plant-growth substances are now available in fertilizers specially prepared for use in flower beds and greenhouses.

Soilless Growth of Plants (Hydroponics, or Chemiculture) · In the growth of plants the soil has a double function: it holds the plant foods, and it provides anchorage for the roots that support the plant. Both functions may be provided for successfully without any soil. The plant may be artificially supported, and the roots may find nourishment in water to which has been added the foods essential to plant growth in

suitable form and concentration. Garden vegetables and flowers may be grown in this way as window gardens or in greenhouses and with surprising results, but this mode of cultivation is not likely to be extended to field crops.

Commercial Fertilizers · As a rule, commercial fertilizers are mixtures of two or more of the essential plant foods. The composition of the fertilizer is adjusted to the crop to be grown and to the character of the soil under cultivation. For example, potatoes thrive best in a soil rich in potassium compounds, while wheat is benefited more by phosphates. These fertilizers are usually sold in bags on which are stamped three figures, such as 2–12–6. The first figure gives the percentage of nitrogen in the fertilizer, the second the percentage of phosphorus (calculated as P_2O_5), and the third the percentage of potassium (calculated as K_2O).

Liming soils. Sometimes a soil becomes sour, or acid, owing to the formation of acids from decomposing vegetable matter or from the oxidation of minerals such as pyrite. Certain plants, such as mosses, sorrel, and huckleberries, will thrive in acid soil, but grass, clover, and grain crops will not. Such soil must be *sweetened* by spreading calcium hydroxide (slaked, or hydrated, lime) or ground limestone upon it to neutralize the acids. The process is called *liming* the soil. An acid soil may be detected by moistening strips of blue litmus and covering them for a few minutes with the moist soil.

Soil Conditioners · Some of the new synthetics, such as the polyacrylates, polyvinylites, and some cellulose derivatives, when used as dressing for soil, are able to stick the clay particles together into crumbs or aggregates and so change a hard, clodlike soil into a soil that is much more suitable for crop growth. These added "conditioners," unlike humus which performs a soil-conditioning function in nature, do not also serve as fertilizers. But the conditioners are not easily washed away, and they are chemically very stable, lasting in the soil for several years. The usefulness of these man-made aids to the control of the tilth seems likely to become very great.

Insecticides and Fungicides

The Problem · Anyone who has had even a little experience in growing plants or animals knows how hard it is to keep them free from organisms that either kill them or impair their growth. So serious are the problems suggested by this experience that our entire food supply is threatened unless they can be solved. The national government and the state experiment stations are constantly carrying on experiments to find effective ways and means of fighting the pests that are a threat. Some of these pests have been brought under control, but others have not. For example,



A Devaney Inc., N Y

Fig. 46-3. Helicopter Dusting Orange Trees with Sulfur

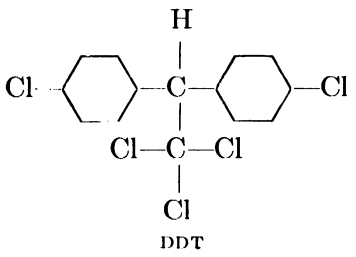
a blight has killed practically all our chestnut trees, and the elms seem doomed to follow unless some way is found to control the disease that is now exacting a heavy toll. Many of these pests are visible insects, such as cattle ticks and aphids, while others, more difficult to combat, are fungi (molds), bacteria, and viruses.

The Attack · The general method of attack is to treat the plants or animals with a spray or dip containing chemicals that kill the destructive organisms. These chemicals vary according to the pest to be conquered. Those used for insects are called *insecticides*; those for fungi, *fungicides*. A few of the most important of these two classes are the following: (1) *Arsenic compounds*, which are largely used as insecticides, include lead arsenate ($Pb_3(AsO_4)_2$), calcium arsenate ($Ca_3(AsO_4)_2$), and Paris green, a complex double salt of copper acetate and copper arsenite. (2) *Lime-sulfur spray* is an aqueous solution of sulfur compounds, chiefly the sulfides CaS_4 and CaS_5. It is made by heating a mixture of calcium hydroxide, sulfur, and water and acts both as an insecticide and as a fungicide. It is widely used, especially in spraying fruit trees. (3) *Bordeaux mixture* is a complex fungicide made by adding calcium hydroxide to a cold solu-

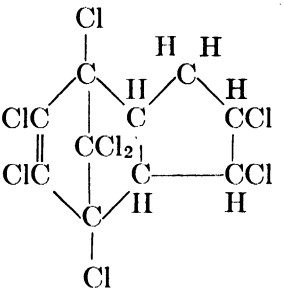
tion of copper sulfate. (4) *Nicotine sulfate* is very poisonous to certain insects, such as aphids and leaf hoppers. (5) A mixture of *cresols* obtained from coal tar (p. 558) acts as an insecticide and is the basis of many common disinfectants. (6) *Hydrocyanic acid* is very effective in keeping citrus fruit trees free from injurious pests.

As all six of these agents are toxic to human beings, and two of them (nicotine sulfate and hydrocyanic acid) very toxic, great care must be taken in the use of them. Two other products have come into use because they are not poisonous to man or to any warm-blooded animal. These are *pyrethrum* and *rotenone*. Pyrethrum is a powder obtained from certain plants belonging to the chrysanthemum family, while rotenone comes from the roots of plants of the derris family. They are insecticides and seem to act by paralyzing the nervous system. The common fly repellents usually consist of a solution of the active principles of pyrethrum dissolved in a paraffin oil.

A product which has proved very efficient against most insects is DDT (dichlorodiphenyltrichloroethane):



DDT



Chlordane

DDT has been used successfully as an insecticide, in the form of either a dust or a spray, for houseflies and lice and for a variety of farm and garden insect pests. It appears to kill by contact and is effective over considerable lengths of time. Other synthetic products, such as chlordane and methoxychlor, which has a structure resembling the molecule of DDT, are said to have excellent properties.

The Health-Purification of Water

Pure Water · We have seen that natural waters are never chemically pure, but always contain more or less mineral and organic matter (p. 113). To obtain chemically pure water from natural waters all foreign matter must be removed, and this is done by distillation. Distilled water has

important uses in scientific investigations, for filling storage batteries, and as a solvent for medicines.

Requirements for a Public Water Supply · When we say that water for drinking purposes is *pure*, we mean that there is nothing in it to endanger health. The menace to health of an impure water is not due to the mineral matter that it may contain, nor to the lifeless organic matter, but to definite kinds of bacteria and other microorganisms that are likely to accompany the organic matter. A safe drinking water must be free from these microorganisms, and should have other qualities as well. In his treatise entitled *Water Supply and Treatment*, C. P. Hoover states that the requirements for a public water supply are as follows:

1. That it shall contain no organisms which cause disease.
2. That it be sparkling, clear, and colorless.
3. That it be good-tasting, free from odors, and preferably cool.
4. That it be reasonably soft.
5. That it be neither scale-forming nor corrosive.
6. That it be free from objectionable gas, such as hydrogen sulfide, and objectionable minerals, such as iron and manganese.
7. That it be plentiful and low in cost.

Bacteria · These are low forms of microscopic life. They exist in countless numbers in the soil, in dust and dirt, in the atmosphere, and especially in refuse matter. They are literally everywhere. There are many different kinds of bacteria. Some of them are of great service; and we grow certain species for definite uses, just as we grow other organisms. Other species are the direct cause of certain diseases. It is known that many transmissible diseases, such as typhoid fever, are due to bacteria, each disease being the result of the growth of a definite kind of organism in the body. It is easily possible for these bacteria to find their way, through sewage from persons afflicted with a disease, into a poorly protected water supply; and it is in this way that typhoid fever is spread. Bacteria are killed by heat, which leads to the common practice of boiling a sample of water to render it safe for drinking. As they are more resistant to cold, however, ice frozen from impure water is not safe for human consumption.

Importance of Purifying Water · An adequate supply of wholesome drinking water is of the utmost importance to a community, and the problem of securing it becomes increasingly difficult as the population increases. Our cities and many of our towns find it necessary to take their water supply from rivers and lakes. With increasing population it is impossible to keep such waters from contamination with sewage and other organic matter, which are natural carriers of disease-producing microscopic organisms.

Effect of water purification on disease. Fig. 46-4 shows the effect of water purification in diminishing the deaths due to typhoid fever in a typical city (Columbus, Ohio). Before the water was purified, typhoid fever was always

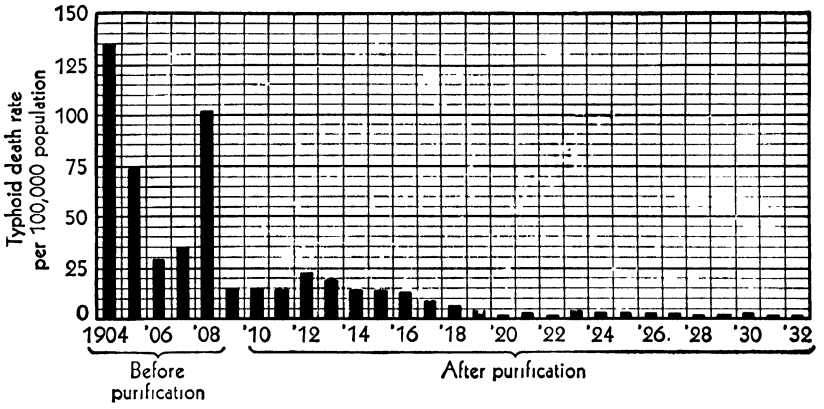


Fig. 46-4. Effect of Water Purification on Death Rate Due to Typhoid Fever

prevalent; for example, in 1904 there were about 135 deaths from this disease for each 100,000 inhabitants. After the construction of a water-purification plant, in 1909, the deaths due to this disease fell off greatly, amounting in 1920 to only 3 for each 100,000 of population; and at present the disease is almost unknown in this city. The purification of the water supply is therefore an important problem.

Purification of Water on a Large Scale · Such processes as boiling and distillation are not practicable in dealing with the large quantities of water required to meet the demands of cities and towns. In Columbus, Ohio, for example, the city water system is drawn upon for an average of 45,000,000 gal daily (about 100 gal per inhabitant), while in Chicago the amount is over 1,000,000,000 gal (250 gal per inhabitant). A number of different methods of purifying water on a large scale are now in use. These methods differ in detail, but all are alike in that the water is treated with chlorine, to destroy any microorganisms present. The amount of chlorine ordinarily added varies from 2 to 5 lb per 1,000,000 gal of water. The different methods are as follows:

1. **Treatment with chlorine alone.** This is the simplest method, but it can be effectively employed only when the natural water used is clear, as is the case in New York.

2. **Filtration through slow sand filters and subsequent treatment with chlorine.** These filters are constructed of sand and gravel, as shown in Fig. 46-5. The water filters through the sand and gravel and passes into

the porous pipe, A, from which it is pumped into the city mains. Some of the impurities are strained out by the filter, while others are decomposed by the action of certain kinds of bacteria which collect in a jelly-like layer on the surface of the filter. Chlorine is added to the filtered water as an extra precaution.

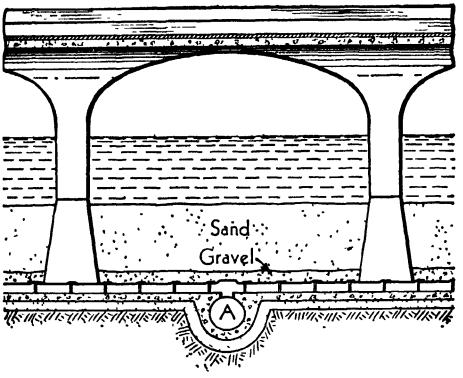


Fig. 46-5. Diagram of a Slow Sand Filter

3. **Treatment with aluminum sulfate, filtration, and subsequent treatment with chlorine.** Most natural waters are basic in character. When aluminum sulfate is mixed with such waters, hydrated aluminum oxide (aluminum hydroxide) is formed (p. 742) as a colloidal dispersion throughout the water. This slowly coagulates and, as it settles, carries down with it any suspended matter present, including bacteria and coloring materials. After the precipitate has settled, the supernatant water is drawn off and run through rapid sand filters. It is then treated with a small amount of chlorine as a final precaution. The rapid sand filters are made of sand and gravel (Fig. 46-6). They have largely replaced the slow sand filters because they are much less expensive and are equally effective when used with water which has been treated with aluminum sulfate. (Other precipitating agents, such as ferrous sulfate, are sometimes used.)

Removal of objectionable tastes and odors in city water supplies. Not infrequently city water supplies acquire a disagreeable taste or odor. This may be due to a number of causes, such as the presence of certain microscopic organisms or algae, dissolved gases, or materials which find their way into the water from industrial plants. Overchlorination may also produce an unpleasant odor and taste. These objectionable qualities may be removed by different methods. The gases present may be removed by aeration. Activated carbon is a very efficient agent for the purpose; the water may be filtered through a bed of granular carbon, or a small percentage of activated carbon may be added directly to the water and, after allowing a short reaction period, be removed by filtration. Objectionable qualities resulting from overchlorination may be remedied by the addition of a small percentage of sulfur dioxide or sodium sulfite.

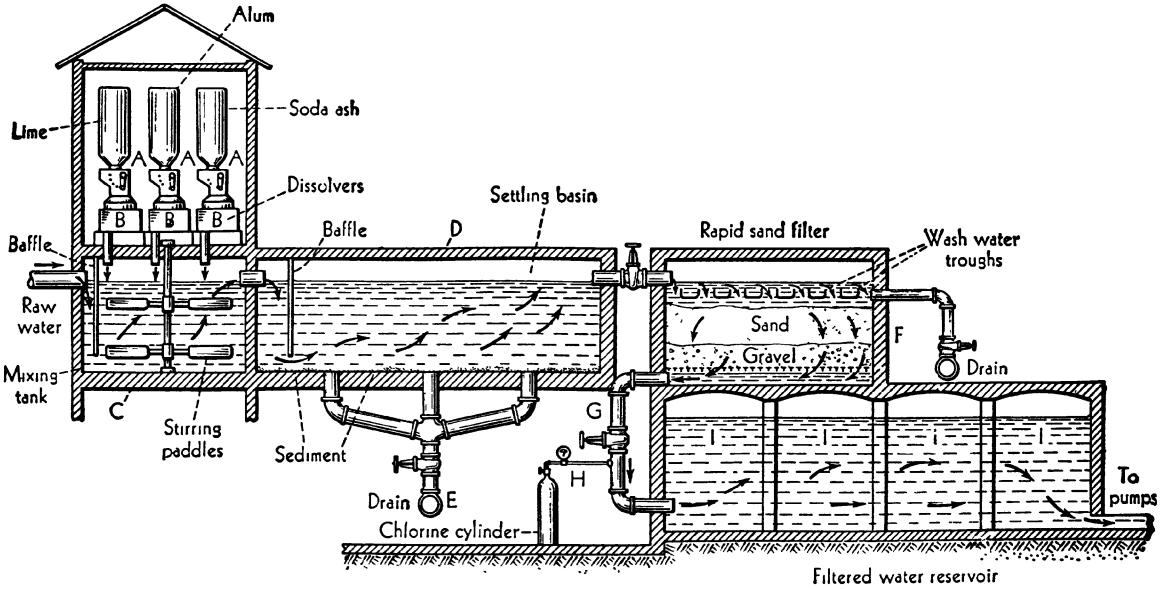


Fig. 46-6. Diagram Showing the Essential Parts of a Plant for Softening and Purifying the Water Supply of a City · The impure raw water enters the mixing tank, *C*, where it is thoroughly mixed with the purifying and softening reagents entering at the top of the tank, as shown in the diagram. The mixture then flows into the settling basin, *D* (see also Fig. 46-7), where the solids formed by the action of the purifying reagents upon the water settle to the bottom and are drawn off through *E* from time to time. The water next flows through the rapid sand filter, *F*, then through the pipe *G* (where the necessary chlorine is added at *H*) into the filtered water reservoir, and from this into the city mains. The rapid sand filters are cleaned by occasionally forcing a stream of water through them in the reverse direction. The water carrying the impurities flows out through the "wash water troughs" into the drain, as shown in the diagram

The Industrial Purification of Water

Softening of Hard Waters · Most of the natural waters have varying percentages of compounds of calcium and of magnesium, derived from contact with various rocks. All such waters are called *hard*. These hard waters are objectionable in many ways. When used for cleansing purposes, much larger quantities of soap are required than with soft waters; and if they are used in steam boilers, deposits are formed, called boiler scale (p. 790). Hence many cities find advantage in softening their water at the same time that they purify it.

The method used to do this involves a modification of the third method described on page 786 for purifying water. Along with the aluminum sulfate there are added sufficient quantities of calcium hydroxide and sodium carbonate to precipitate the calcium and magnesium present (Fig. 46-6). The calcium and magnesium in hard waters are present as ions, together with the acid carbonate ion and the sulfate, chloride, and nitrate ions. The addition of the base calcium hydroxide changes the acid carbonate ions to carbonate ions, which brings about the precipitation of insoluble calcium carbonate:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3 + 2\,H_2O$$

At the same time the hydroxyl ions of the base bring about the precipitation of magnesium as magnesium hydroxide:

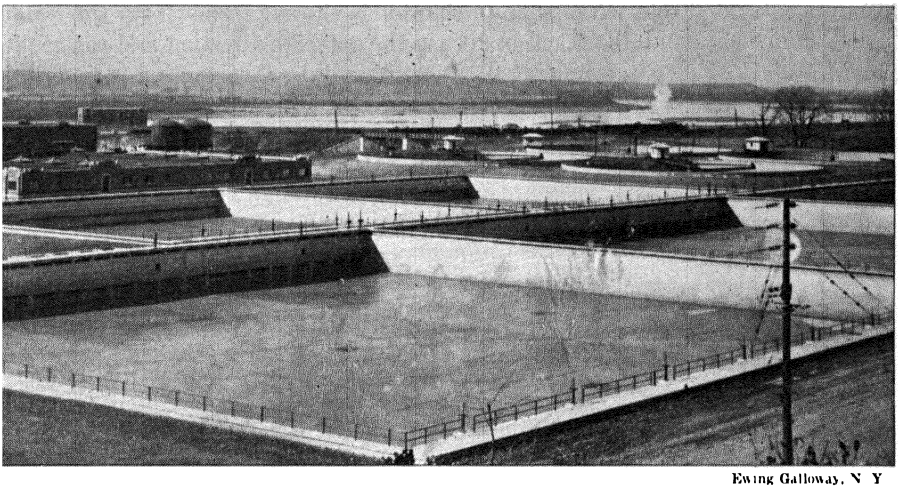
$$Mg(HCO_3)_2 + 2\,Ca(OH)_2 \longrightarrow Mg(OH)_2 + 2\,CaCO_3 + 2\,H_2O$$
$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$$

Any calcium ions remaining in the solution, either from those originally present or from the calcium hydroxide added, are removed by the addition of sodium carbonate:

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2\,NaCl$$
$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

It will be seen from these equations that the calcium is precipitated as the carbonate, and the magnesium as the hydroxide. These two compounds are practically insoluble in water and settle out as the water slowly flows through reservoirs called *settling basins* (Fig. 46-7). It is also evident from the equations that waters softened by this process contain sodium salts, but the presence of these is not objectionable unless the water is used for special purposes; they have no effect on soap.

Some idea of the economy resulting from the softening of city water supplies may be had from the fact that the softening of the city water in Columbus, Ohio (population 340,000), has effected an estimated saving in soap alone amounting



Ewing Galloway, N Y

Fig. 46-7. Settling Basins of the Kansas City Water Works

annually to more than $500,000. An extensive investigation proved that in Illinois the average city of 40,000 inhabitants wastes about 1 ton of soap daily because of the hardness of the water, to say nothing of the loss of heat due to the formation of boiler scale.

The use of sodium hexametaphosphate in the treatment of water. When water is softened by the addition of calcium hydroxide and sodium carbonate, the reaction gradually slows down, so that several days may be required for completion. As a result, the water, after it enters the city mains, still contains a small percentage of calcium and magnesium salts, which are slowly deposited in the pipes through which the water flows. In time this causes trouble by clogging the pipes; and this is especially true when the water is used in steam boilers, since heat hastens the final reactions. Hall, a water chemist of Pittsburgh, has found that the addition to the water, either before or after it passes through the filter, *F* (Fig. 46-6), of a small percentage of sodium hexametaphosphate ($(NaPO_3)_6$), known by the trade name of Calgon, prevents further precipitation, and so the pipes are kept free from deposits. Just how the metaphosphate acts to prevent precipitation is not known. Only a very small percentage of it is required. For example, in Columbus, Ohio, only 2 lb of the metaphosphate per million gallons of water is required to prevent further precipitation. Solutions of the hexametaphosphate, as well as of sodium pyrophosphate ($Na_4P_2O_7$), are effective in dissolving scale after it has formed—for example, in cleaning the radiator of an automobile.

The zeolite process for softening water. The name *zeolite* is given to a mixture of complex sodium-aluminum silicates found in nature and also prepared synthetically for use in softening water. The sodium of the zeolite is replaced by the calcium and magnesium ions in hard waters when such waters are brought into contact with the zeolite, thus:

$$Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2 + CaCl_2 \rightleftarrows CaO \cdot Al_2O_3 \cdot 2\,SiO_2 + 2\,NaCl$$

If now a saturated solution of sodium chloride is allowed to flow over the resulting calcium compound, the reaction goes in the opposite direction and the zeolite is regenerated. In other words, the reaction is reversible and may be made to go in either direction by increasing the concentration of the appropriate compound. In softening water by this process the zeolite is placed in a long drum and the hard water passed through the drum (Fig. 46-8). The apparatus is built in duplicate, so that the material in the one drum may be regenerated while that in the other drum is being used for softening the water. It is evident that water softened in this way will contain sodium salts, but these have no effect on soap.

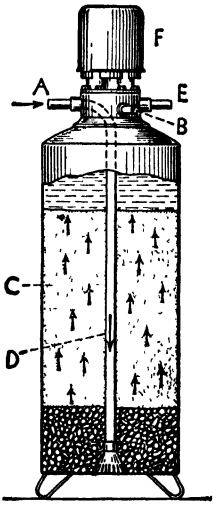


Fig. 46-8. A Diagram of the Zeolite Process for Softening Water · The hard water enters at *A* and flows to the bottom of the container through the pipe *D*. It is then forced upward through the zeolite, *C* which removes the calcium and magnesium ions. The resulting soft water flows out through the pipe *B*. From time to time a solution of sodium chloride, forced in at *E*, regenerates the zeolite

While this method has been used largely for softening water on a small scale, especially in individual homes, it is now coming into use for softening city water supplies. It is not so efficient as the lime-soda process for removing calcium and magnesium when these are present as the acid carbonates.

Ion-exchange Resins · Many high polymers, both natural and synthetic, will adsorb either cations or anions. For example, cellulose, in the form of cotton, will remove ferric ions from solution. In recent years synthetic high polymers have been made in which this effect is as pronounced as it is in the zeolites, and can be made considerably more selective. In general, one type of resin removes cations and another removes anions, so that, by a judicious use of a series of such adsorbents, water, even sea water, can be made practically as pure as by distillation.

Boiler Scale · When water which contains certain salts in solution is evaporated in steam boilers, a hard, insoluble material called *scale* deposits in the boiler. The formation of this scale may be caused by

1. **Deposit of calcium sulfate.** This salt, while sparingly soluble in cold water, is almost completely insoluble in superheated water. Consequently it is precipitated when water containing it is heated in a boiler.

2. **Decomposition of acid carbonates.** As we have seen, calcium acid carbonate and magnesium acid carbonate are decomposed on heating, forming insoluble normal carbonates:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

3. **Hydrolysis of magnesium salts.** Magnesium chloride and, to some extent, magnesium sulfate undergo hydrolysis when superheated in solution, and the sparingly soluble magnesium hydroxide is precipitated:

$$MgCl_2 + 2\ H_2O \longrightarrow Mg(OH)_2\downarrow + 2\ HCl$$

The scale adheres tightly to the boiler tubes in compact layers (Fig. 46-9) and, being a nonconductor of heat, causes much waste of fuel. It is very difficult to remove, owing to its hardness and resistance to reagents. Thick scale sometimes cracks, and the water, coming in contact with the overheated iron, may cause an explosion. Moreover, the acids set free in the hydrolysis of the magnesium salts attack the iron tubes and rapidly corrode them. For these reasons water containing such salts should be softened before being used in boilers.

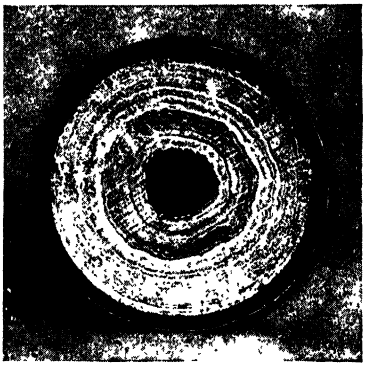


Fig. 46-9. Cross Section of a Boiler Tube, Showing the Deposit of Scale

QUESTIONS

1. Upon what does the fertility of a soil depend?

2. Name the different ways of increasing the fertility of a soil.

3. Would the chemical analysis of a soil tell the whole story as to its fertility?

4. We have to use at least three different insecticides in spraying different trees and plants. Why are so many necessary?

5. What properties would constitute the ideal insecticide?

6. Are any insecticides known that are poisonous to insects but not to human beings?

7. Give different meanings applied to the term *pure water*.

8. (*a*) What are the common impurities present in ordinary waters? (*b*) To which of these is hardness due?

9. (*a*) What mineral constituents are commonly present in natural waters? Suppose you wished to soften such waters: (*b*) What chemicals would be required? (*c*) Write the equations for the reactions that would take place in the process.

10. State the advantages to be gained by a city in using pure, soft water.

11. How do you account for the fact that the sodium compounds formed in the softening of water have no action on soap?

12. (*a*) Why are chemists necessary in all water-purification plants? (*b*) What are their particular duties?

13. Point out how it is possible to remove calcium compounds from water by adding another calcium compound.

14. Why should an ammonia fertilizer or a natural manure not be mixed with *burned* lime or the two spread on a field at the same time?

PROBLEMS

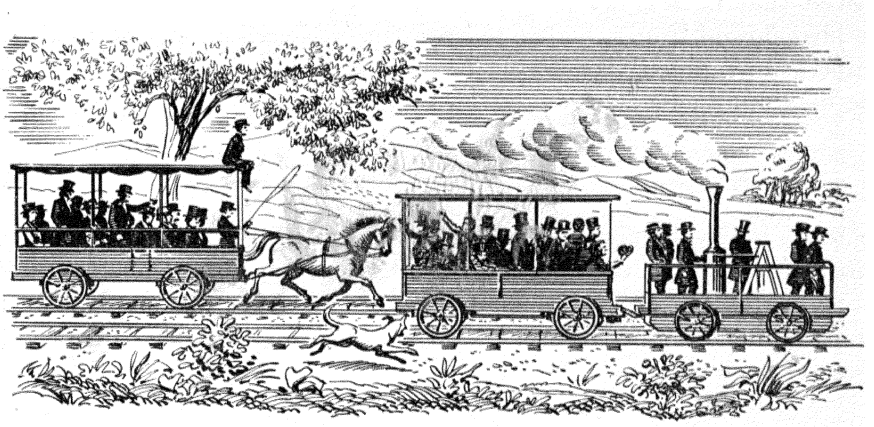
1. Ordinary rock phosphate, used in making fertilizers, contains about 70 per cent of calcium phosphate. (*a*) What weight of sulfuric acid containing 45 per cent of H_2SO_4 is necessary to convert 1 ton of the rock phosphate into superphosphate of lime? (*b*) Why is such treatment necessary?

2. Lead arsenate, a common insecticide, is made by treating lead acetate with sodium arsenate. What weight of each of these compounds is necessary for the preparation of 100 lb of lead arsenate?

3. A certain city uses 30,000,000 gal of water daily. Suppose that this water contains 50 g of calcium acid carbonate and 20 g of calcium sulfate in 100 gal of water. What compounds and what weight of each would be required to soften the daily water supply?

CHAPTER 47

FUELS AND SOURCES OF POWER



Introduction · For many thousands of years men warmed themselves before wood fires. The use of fuel as a source of power, however, for doing useful work has come only lately into our civilization. Until the nineteenth century men did their work with muscles, either their own, their slaves', or those of their horses or other beasts of burden. Work was done by windmills and water wheels from Greek and Roman times, and transportation by sailboat was known from the dawn of history. But man's first practical device for converting fuel energy into mechanical energy was James Watt's steam engine, and the steam engine was not available until the early 1800's to drive factory wheels and boats and locomotives.

During the following 150 years the use of fuels as sources of mechanical energy increased at a tremendous rate. Today the world's energy requirements are approximately 40 trillion (40,000,000,000,000) horsepower-hours annually. Not all of this energy goes into engines; about half of it, and in some regions 90 per cent of it, is spent in keeping people warm. In a country as highly industrialized as the United States we consume, in a year like 1951, about 14 trillion horsepower-hours and this means that every one of our 175,000,000 people has, on the average, an equivalent of 40 horses or 900 slaves working for him. Only one quarter of this country's energy is used for space heating and for cooking foods.

Efficiency of Conversion of Heat into Work · The mechanical engineers, trying to improve the performance of the early steam engines, were anxious to know just what maximum efficiency a steam engine could

have in converting heat into work. Could the engine change all the heat that it received into useful work? If not, then what fraction of it? The answer to this question was given in 1824 by the brilliant 28-year-old Nicolas Carnot, the son of Napoleon's quartermaster general. Carnot showed that heat could be converted to mechanical energy only when the heat flowed from a higher temperature through an engine to a lower temperature—much like water flowing downhill over a water wheel. The maximum efficiency was given by the expression

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2}$$

where T_2 is the temperature of the hot steam in the boiler and T_1 is the temperature of the much cooler spent steam in the condenser. (The temperatures are on the absolute scale.) Carnot's efficiency equation applies to heat engines of every kind, and it has been very helpful in the design of such engines.

One of the most efficient steam engines ever built, operating between a boiler temperature of about 483.6° A and a condenser temperature of 316.3° A, had a maximum theoretical efficiency of about 34 per cent (483.6–316.3)/483.6. Actually, the engine showed a conversion of only 25 per cent of the heat into work, because of friction and other losses. Ordinarily, steam engines run at much lower efficiencies, from 8 to 10 per cent, though some gasoline engines, turbines, and Diesels, operating at considerably higher temperatures, do much better, reaching actual efficiencies of 20, 30, and 35 to 40 per cent, respectively.

The surface of the sun, at a temperature of 6000° C, radiates heat to the earth, which has an average temperature of 10° C; this heat could in principle be converted into mechanical or electrical energy at very high efficiency, about 95 per cent (6273–283)/6273.

The Sun as a Main Source of Energy · Practically all our energy comes directly or indirectly from the sun. *Directly*, we receive from sunlight an average of about 1 to 2 calories per minute on a square centimeter of the earth's surface, and so receive on a square yard 138 to 275 calories per second. If we could transform about 250 calories of such heat into electrical or mechanical energy at the high efficiency we have just mentioned, we could obtain the equivalent of about 1000 watts, or $1\frac{1}{3}$ horsepower, from the sunshine falling continuously on 1 square yard of the earth. We do not yet know how to accomplish such a transformation efficiently; but the problem of trapping solar energy is one of mankind's most pressing problems.

The energy that we obtain *indirectly* from the sun comes from natural

sources of stored energy, namely, from waterfalls and wind and from fuels, from recently grown plant materials, especially wood, or from fossil fuels, such as coal, oil, and gas.

Two sources of heat not dependent either directly or indirectly on sunshine, are (1) the subsurface heat of the earth, coming from disintegration of radioactive elements present there, and (2) the nuclear energy that man is now learning how to release and control.

Renewable and Nonrenewable Sources of Energy · Undoubtedly the sun is fired by nuclear energy, liberated largely by the fusion of hydrogen nuclei to form helium nuclei (pp. 358–363), as in one form of the hydrogen bomb. Thus *all* our ultimate sources of energy are nuclear. It is estimated that the sun uses up about 1 per cent of its hydrogen in a billion years; and the expectation is that it will be giving out heat radiation of essentially the present intensity for several billion years to come.

Sunshine, or solar energy, is therefore an inexhaustible source; and the sources of energy derived from sunshine, such as waterfalls and wind, and plant materials, more especially wood and peat, recently derived by photosynthesis, are renewable. But the fossil fuels, coal, gas, and oil, also containing stored solar energy, are not renewable; nor are uranium and thorium, from which fissionable materials may be prepared.

Let us now consider, in order, the nature of these several sources of energy and power with respect to their origin, our manner of using them, and their recoverable reserves. We shall save solar energy and photosynthesis for the last.

Water Power, Wind, and Tide · The heat of sunshine causes the evaporation of enormous quantities of water every day from the surface of the sea and other bodies of water, and from the leaves of plants. (About 590 calories of heat is required to evaporate 1 gram of water at 10°.) Water vapor, rising in currents of warm air into the atmosphere, is condensed to rain; and rain water, on the mountains and hills, gathers in streams and rushes down to the sea. The kinetic energy of flowing water can be transformed into electrical energy by means of water wheels or turbines coupled to generators. The electrical energy is distributed over copper wires to our homes and factories. Many industries which require a cheap and readily available supply of energy tend to concentrate in regions near large waterfalls, as at Niagara Falls. Less than 5 per cent of the power consumed annually in the United States is water power; however, 80 per cent of our definitely realizable water power remains undeveloped.

Although it seems likely that wind power could supply as much as 15 per cent of the world's requirement of 40 trillion horsepower-hours,

actually the windmills in the United States generate yearly only about 450 million horsepower hours. This is less than 0.1 of 1 per cent of our total water power, and it is said that our electric fans consume more than 3 times as much energy as the windmills yield.

Tide power could in principle satisfy half the world's needs, but it cannot presently compete economically with other sources of energy.

Plant Materials, Especially Wood and Peat · In times of overproduction, both wheat and corn have been burned as fuel, and various kinds of grains are used in fermentation processes to produce fuel alcohol. Of the various available plant materials, wood has been the prime fuel. Its calorific value is good, and it is often to be found near at hand. Although it contributes only about 5 per cent of our total energy (putting it on a par with water power and anthracite coal), it is an important part of the store of fuel in some localities. In the United States in 1800 it made up about 95 per cent of the total consumption. Several peoples have made terrific inroads on their woodlands; for instance, the Chinese in making the bricks (about 300 B.C.) for their Great Wall (more than 2000 miles long, 20–50 feet high, and 15 to 25 feet wide), almost wiped out their forests. This is easily believable once one realizes that about 150 cubic feet of wood is needed to make 1 cubic foot of burnt brick. England was barely saved from the almost total destruction of her forests by the substitution of coke for the enormous quantities of charcoal used in blast furnace operation.

Peat is formed from the decomposition of aquatic plants such as reeds, rushes, sedges, and mosses, and accumulates at the rate of about 1 inch a year in bogs 10 feet or more deep. When dried, it shrinks enormously, but makes a good fuel, having about half the calorific value of bituminous coal (p. 804). It is produced several times as fast as wood on an equal area. It is produced in several countries, about 6 million tons annually in Ireland and 30 million in Russia. Most of our own peat is found in Minnesota, and there is said to be enough of it to meet our national energy requirement for about 4 years.

Charcoal · Charcoal is an excellent fuel. It burns with a small, hot, clean flame, like an ember. Its calorific value is given in the table on page 804.

It is made by heating wood in the absence of air, and in modern practice the volatile products, mainly methyl alcohol, acetic acid, and acetone, are condensed and saved. The mineral constituents of the wood remain in the charcoal. The relative composition of coal, coke, wood, and charcoal is represented approximately by the following analyses of typical samples:

PERCENTAGE COMPOSITION OF SOME SOLID FUELS

	TOTAL CARBON	HYDROGEN	OXYGEN	NITROGEN	SULFUR	ASH	TOTAL VOLATILE MATTER
Coal (anthracite)	82.04	2.70	3.50	0.77	0.74	10.25	5 to 8
Coal (semi-bituminous)	82.71	4.43	3.98	1.33	0.68	6.87	18 to 20
Coal (bituminous)	78.03	4.99	6.11	1.53	1.05	8.29	30 to 35
Wood	40.00	7.20	50.70	0.80	Traces	1.30	50 to 60
Coke	89.00	Traces	Traces	Traces	0.80	10.20	Traces
Charcoal	97.00	Traces	Traces	Traces	Traces	3.00	Traces

Destructive Distillation · The process of decomposing such substances as coal, wood, and bones by heating them in the absence of air is called *destructive distillation*; and coke, charcoal, and bone black are, respectively, the solid products of such distillation.

Coal · Coal is a solid fossil fuel. The fuel economy of the United States, based largely on wood in 1800 (p. 796), had become more and more dependent on coal until, about 1890, half of its required energy was supplied by coal. Coal's biggest year was in 1920, when it furnished 64 per cent of the nation's energy. Now, however, it has been partially displaced by oil and gas, and supplies less than 50 per cent of the total energy. The world's production is currently about 2.5 billion tons. Our own production in 1953 was about one-fifth as much—483 million tons—and of this, 453 million tons were bituminous and 30 million tons anthracite. The chief coal-producing districts of this country include West Virginia, Pennsylvania, Illinois, Kentucky, and Ohio.

Origin of Coal · Coals of various kinds have been formed from vast accumulations of vegetable matter in peat bogs, which became covered with water and earthy material and were protected from the usual kind of oxidation. This vegetable and woody debris, probably like peat, and largely cellulosic—$C_6H_{10}O_5$ (Chapter 30)—is supposed to have undergone a slow chemical change involving the evolution of carbon dioxide, carbon monoxide, methane, and water, with a gradual decrease in its oxygen content and a gradual increase in the percentage of free carbon. The changes in composition (percentage C, H, O), from cellulose through lignite and bituminous coal to anthracite and graphite, are shown in the table on page 798. The pressure exerted by the overlying layers of accumulated earthy material or by faulting rock strata may have played some role in the process.

Uses of Coal · There are several different purposes for which we use coal. (1) When coal is the fuel to be used in furnaces for space heating,

	VARIOUS STAGES	APPROXIMATE PERCENTAGE COMPOSITION (ASH-FREE BASIS)		
		C	H	O
PROBABLE STAGES IN THE FORMATION OF COAL FROM CELLULOSE	Cellulose	44.4	6.3	49.3
	Peat	62.0	6.0	32.0
	Lignite	73.0	5.5	21.5
	Subbituminous	80.0	5.5	14.5
	Bituminous	87.0	5.5	7.5
	Semibituminous	92.0	5.0	3.0
	Semianthracite	94.5	3.5	2.0
	Anthracite	96.0	2.5	1.5
	Graphite	98–100		

and for firing boilers for the generation of steam, anthracite, or *hard* coal, made up largely of free carbon, is a very satisfactory fuel, especially if the need is for as nearly smokeless a fuel as possible. However, bituminous, or soft, coal contains much more volatile and resinous material than does anthracite, and is even more desirable, except for its smokiness, because it burns more easily and its calorific value is higher. (2) When some bituminous coals are heated strongly out of contact with air (Fig. 47-1) the temperature rises, destructive distillation occurs, various volatile matters escape, and a residue of hard, strong *coke* is left. As just intimated, not all coals, even the bituminous, are *coking coals*. It seems that only those bituminous coals that contain a certain minimum amount of resinous materials will form the hard, metallurgical coke so important in the manufacture of iron and steel. (3) Coal can be converted, by several types of processing, into liquid and gaseous fuels, and here, too, the bituminous coals are most satisfactory.

How Long Will Our Coal Last? · It is extremely difficult, of course, to do more than make a rough guess at the quantities of coal underground. But the trend of several surveys is to cut the estimated life expectancy of our coal reserves in this country from between two and three thousand years to about one tenth as long. The life of our deposits will depend not only on the actual amount of coal in the coal veins, but also on the rate at which we consume it. If, as our reserves of petroleum and natural gas begin to fade, we lean more heavily on coal as the raw material out of which synthetic liquid and gaseous fuels can be made, our coal reserves will be depleted all the more rapidly. Will they last through the next century? It is to be hoped that we may become wise enough to treasure more dearly our coal, as well as oil and gas, for the chemical substances that we can obtain from them, and learn to depend on some renewable source or sources for our huge energy expenditures.

Fuel Gases · Several gases are commonly employed as sources of heat, light, and power, including (1) coal gas, (2) water gas, (3) producer gas (all three made from coal or coke), and (4) natural gas.

1. **Coal gas.** It has been known for several centuries that when bituminous coal is heated out of contact with air, combustible gases are formed; indeed, gases obtained in this way were used for street-lighting in London as far back as 1812, and in Baltimore in 1817.

The Manufacture of Coal Gas. The manufacture of coal gas is represented in a diagrammatic way in Fig. 47-1. The coal is introduced into rows of closed retorts, *A*, *A*, *A*, and heated. A delivery pipe leads from the top of each of the

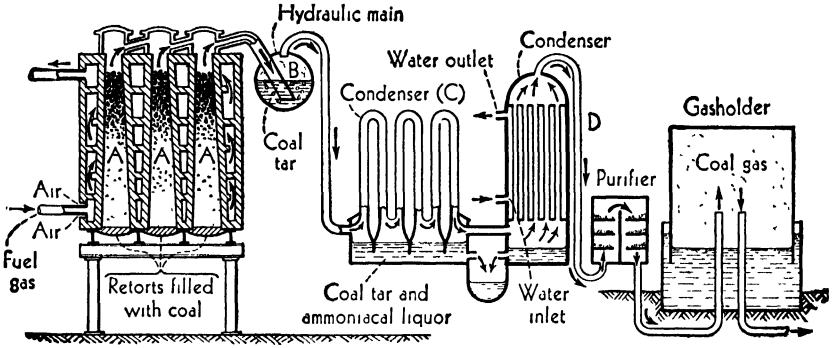


Fig. 47-1. Diagram Illustrating the Manufacture of Coke and Coal Gas

retorts into a large pipe, *B* (known as the *hydraulic main*). The heat brings about complex changes in the coal, which result in the formation of a large number of compounds. Those that are volatile escape through the delivery pipe into the hydraulic main. At the lower temperature of the main, portions of those products that are solid or liquid at ordinary temperatures condense in the form of a dark liquid called *coal tar*. The gases pass on into the *condenser*, *C*, in which they are cooled to such an extent that any tar carried with them is largely deposited. Along with the tar there is condensed a liquid (chiefly water) containing ammonia in solution and known as *ammoniacal liquor*. The gas is then led into a large iron drum, *D*, fitted with copper tubes, through which the gas passes. The tubes are kept cool by running water, and further condensation of vapors takes place in them. From the drum, *D*, the gas passes into the purifier, where it comes into contact with lime or iron oxide, which removes any sulfur compounds still remaining. The gas then enters the large gas holder, from which it is distributed to consumers.

The great bulk of the carbon remains in the retort as *coke* and as *retort carbon*. The yield of gas, tar, and soluble materials depends upon many factors, such as the composition of the coal, the temperature employed, and the rate of heating. One ton of good gas coal yields approximately 10,000 cubic feet of gas, 1400 pounds of coke, 120 pounds of tar, and 20 gallons of ammoniacal liquor.

Not only is the ammonia obtained in the manufacture of the gas of great importance, but the coal tar is the source of many very useful substances (p. 553).

2. Water gas. Water gas is essentially a mixture of carbon monoxide and hydrogen. It is manufactured by passing superheated steam over very hot anthracite, other coal, or coke, the chief reactions being expressed in the following equations:

$$C + H_2O \longrightarrow CO + H_2 - 26{,}990 \text{ cal}$$
$$CO_2 + C \longrightarrow 2\,CO - 41{,}530 \text{ cal}$$

The common industrial process is intermittent. The fuel is burned with a forced draft in a suitable furnace until it is very hot. The air is then shut off, and the steam is turned on until the temperature falls to about 1000°, thus reversing the process. The fall in temperature is rapid, partly because of radiation and the cooling occasioned by the steam, but largely because of the endothermic character of the reactions. The gas so formed contains the nitrogen which was in the furnace when the steam was admitted. A recently developed continuous-feed process uses powdered coke or powdered coal.

Water gas burns with a pale-blue, nonluminous flame. Among industrial fuel gases only acetylene gives a hotter flame. Water gas is very poisonous and especially dangerous because it has no odor.

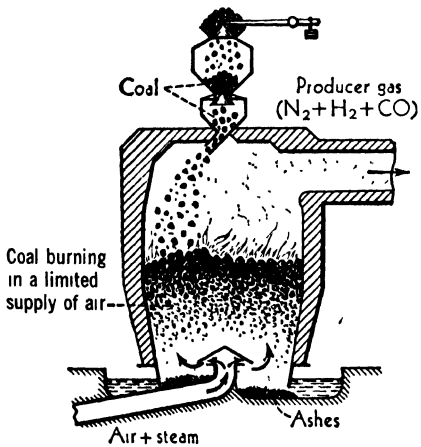


Fig. 47-2. Diagram Illustrating the Manufacture of Producer Gas

3. Producer gas. Producer gas is used in connection with many metallurgical furnace operations and also as a fuel for gas engines. It is made by burning coal in a mixture of air and steam under such conditions that the resulting products are largely carbon monoxide and hydrogen (Fig. 47-2). It also contains the nitrogen present in the air used, and this detracts from its fuel value. It can, however, be made from coal of a poor quality, even from lignite; and as gas engines run well with this gas, it furnishes the most economical method for utilizing low-grade coal for power. Producer gas is used not only as a fuel but also as a source of the nitrogen and hydrogen used in making ammonia by the Haber process (pp. 397, 443). When it is

desired for this use, an excess of steam is added, and this converts the carbon monoxide into the dioxide, which is then removed by dissolving it in water.

4. **Natural gas.** Like petroleum, natural gas is obtained by boring wells into gas-bearing strata. It is usually associated with petroleum and is composed chiefly of methane, with small percentages of other hydrocarbons. The methane content averages about 80 per cent, although in the gas from some fields it may run as high as 90 per cent. Nitrogen is generally present, but usually in very small quantities. Thus the natural gas from the region of Fort Worth, Texas, contains as much as 38 per cent of nitrogen, while the methane content is about 50 per cent. It is interesting that natural gas rich in nitrogen usually contains about 1 per cent of helium.

Natural gas is an ideal fuel and is piped for hundreds of miles from the gas fields to cities. It supplies about 20 per cent of our total energy. It burns with a flame of moderate luminosity. It has a high heat of combustion—much higher than that of coal gas—as shown in the following equation:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 210{,}800 \text{ cal}$$

Comparative Composition of Gases · The figures in the table below are the results of analyses of average samples; but since each kind of gas varies considerably in composition, the values are to be taken as approximate only.

AVERAGE PERCENTAGE COMPOSITION OF GASES BY VOLUME

	NATURAL GAS	COAL GAS	WATER GAS	ENRICHED WATER GAS	PRODUCER GAS
Hydrogen (H_2)	—	52.5	52.88	32.0	21.1
Methane (CH_4)	90.7	30.0	2.16	13.1	4.0
Ethane (C_2H_6)	3.8	0.8	—	2.9	—
Ethylene (C_2H_4)	—	2.0	—	9.8	—
Carbon monoxide (CO)	—	6.8	36.80	29.8	19.8
Carbon dioxide (CO_2)	—	1.7	3.47	4.8	6.8
Nitrogen (N_2)	1.0	3.5	4.69	1.3	48.3
Oxygen (O_2)	—	0.6	—	—	—
Other hydrocarbons	4.5	2.1	—	6.3	—

Petroleum and Gasoline · The oily liquid *petroleum* is a mixture of various hydrocarbon substances. It is separated into its components by fractional distillation (p. 194). The composition of petroleum varies somewhat with the locality of the oil wells from which the petroleum is obtained; but the composition of a representative sample is indicated

in the diagram of Fig. 47-3. An average of approximately 7,000,000 barrels of petroleum is consumed daily in the United States. Of the petroleum products, *gasoline* is the one for which there is the greatest demand, to supply the fuel for over 55 million automobiles in this country. The quantity of *fuel oil* that is used to drive Diesel engines, to heat homes, and to heat furnaces in industrial operations is very large. The oil industry has indeed become a major industry.

Fractional distillation alone will separate petroleum into the various fractions shown in Fig. 47-3. Many other useful products may be obtained by chemical processing of the petroleum. One of the most important of these processes is that of "catalytic cracking," used to produce gasoline. The cracking of a molecule is the decomposition of the molecule into smaller pieces. The hydrocarbon molecules that are present in the kerosene, fuel oil, and paraffin fractions of petroleum (Fig. 47-3 and table on page 511) decompose, when heated to a relatively high temperature, into smaller molecules. If the temperature is sufficiently high, the molecules will decompose completely into carbon and hydrogen; but, with controlled heating, the molecules may be cracked approximately into halves or into thirds, or into the molecules of pentane, hexane, heptane, and octane, present in gasoline. In this way the yield of gasoline from petroleum can be doubled or trebled; in fact, the yield can be made as high as 85 per cent or higher. Some cracking processes operate also at high pressures, and catalysts are generally used. In the *Houdry cracking process* the vapor of the petroleum oils is forced over a synthetic aluminum silicate catalyst at a temperature of about 450° and at a pressure of 1 to 3 atmospheres.

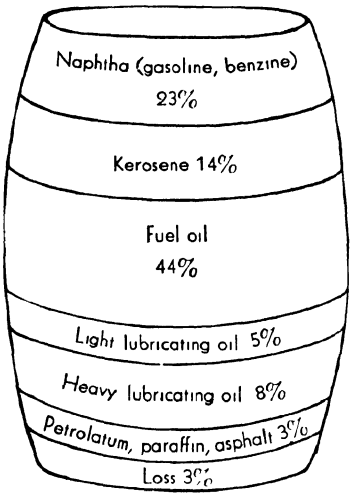


Fig. 47-3. Diagram Showing the Per Cent of Various Products Obtained by the Direct Fractionation of Petroleum

In the so-called "re-forming" process, the long straight chains of the petroleum-oil molecules are broken into small fragments, or radicals, which are then catalytically re-formed into molecules which are highly branched and are in the gasoline range of sizes. The branched-chain hydrocarbons have the best antiknock properties (p. 596).

Methods of Obtaining Future Supplies of Gasoline · The "proved reserve" of petroleum, based on data of 1950, is about 29 billion barrels

for the United States and 80 billion barrels for the world. Guesses have it that the ultimately producible reserves may be a further 20 billion barrels for the United States. At any rate, it now appears that our domestic reserves of petroleum are not adequate to allow a continued production of petroleum products, especially of gasoline, at a rate that can keep pace with our rapidly increasing needs. We may increase our imports of petroleum from abroad, from Mexico, Venezuela, Iran, or other countries, or we may, at the same time, take serious thought for the possibility of developing methods for extracting liquid hydrocarbon fuels from our oil-bearing shales or for manufacturing liquid hydrocarbon fuels from coal.

1. **Oil from shales.** In Colorado and some other Western states there are enormous deposits of shales (fossil rocks). When these are heated, complicated reactions occur, which result in the formation of a number of valuable products, including a petroleum-like liquid. The total reserves of bituminous or oil substances contained in these shales are tremendous, but the cost of the finished product is likely to be high. For example, a gallon of gasoline from shales might cost as much as ten cents more than our present gallon of gasoline.

2. **Hydrogenation of coal.** A method for preparing petroleum-like products by the hydrogenation of coal was developed by the German chemist Bergius. The method consists in treating very finely powdered coal, dispersed in oil as a slurry, with hydrogen under high pressure, in contact with a suitable catalyst, at a temperature of about 500°. Under these conditions various useful products are formed, including lubricating oils, kerosene, and gasoline. The quality of the gasoline so produced is good; but the cost is likely to be relatively high, chiefly because of the large cost of the installation for manufacture.

3. **Fischer-Tropsch process.** Another method for converting coal (or coke) into gasoline and other petroleum-like products is the Fischer-Tropsch process. The coal (or coke) is first made to react with steam, in the water-gas reaction (p. 800), to yield carbon monoxide and hydrogen. A mixture of carbon monoxide and hydrogen, in proper proportions, when passed, at proper temperatures and pressures, over suitable catalysts, can be converted into hydrocarbons, either gasolines or fuel oils or lubricating oils. The temperatures vary from 150° to 500°, and the pressures vary from 5 to 500 atmospheres. Catalysts that have been employed are cobalt, cobalt-thorium oxide, aluminum oxide, and molybdic oxide on activated charcoal; and aluminum chloride has been used in the synthesis of lubricating oils. One theory of the mechanism of the reaction is that the carbon monoxide (CO) molecules are converted to

methylene groups ($-CH_2-$), which arrange themselves into chains on the various types of catalytic surfaces.

Heat of Combustion of Hydrocarbons · The heat of a chemical reaction may be measured in a calorimeter (p. 584), and the amount of heat liberated or absorbed (for 1 mole of reacting substance) may be indicated in the equation for the reaction. The combusion of a hydrocarbon is an exothermic process. For example, the complete burning of 1 mole of liquid *n*-heptane in oxygen, to form carbon dioxide and water, liberates 1150.8 kcal.

$$C_7H_{16} + 11\ O_2 \longrightarrow 7\ CO_2 + 8\ H_2O + 1150.8\ \text{kcal}$$

The Calorific Value of Fuels · The various materials used as fuels differ much in the heat which they give off when burned. While many other factors are concerned in the value of a fuel, the chief one is its heat of combustion. *The heat evolved by the combustion of one gram of a (solid or liquid) fuel is called its calorific value.* Sometimes the heat developed by 1 pound of a fuel is expressed in British thermal units (Btu). (1 Btu = the heat required to raise 1 pound of water 1° F = 251.5 cal.) In large contracts the price paid for a fuel is, as a rule, based on its calorific value, as well as on its adaptability to the desired use. The table below gives some average values for a few common fuels in terms of calories per gram and British thermal units per pound for the solids and liquids, and in terms of British thermal units per cubic foot for the gases.

CALORIFIC VALUES OF SOME COMMON FUELS

SOLID AND LIQUID FUELS		
Fuel	Cal/g	Btu/lb
Wood	4,000	7,300
Charcoal (willow)	7,520	13,530
Peat (as cut)	1,110	2,000
Peat (air-dried)	4,170	7,500
Lignite	5,000	9,000
Bituminous (Ohio)	7,000	12,730
Semibituminous (West Virginia)	7,470	13,590
Semianthracite (Virginia)	6,020	10,960
Anthracite (Pennsylvania)	7,340	13,350
Petroleum, kerosene, gasoline	10,300	18,540

GASEOUS FUELS	
Fuel	Btu/cu ft
Natural gas	1,110
Coal gas	555
Water gas	300
Producer gas	155

Nuclear Energy

Nuclear Energy · The general subject of nuclear energy, produced by the fission or fusion of atomic nuclei, was introduced in Chapter 21; and a discussion of the atomic and hydrogen bombs and their terrible effects on man and his cities was given, as well as a brief account of what the helpful new tool, the radiotracer, can mean in chemical and medical research.

The Reactor · Nuclear energy for industry is produced in a *reactor*, formerly called a pile. A reactor, as we have already said (p. 364), is essentially a "tamed bomb," in which the fission chain reaction (p. 361) is controlled so that the energy is released slowly instead of explosively.

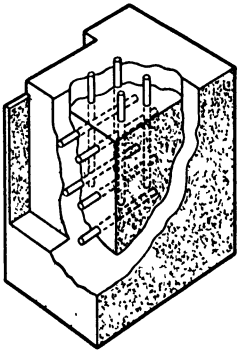


Fig. 47-4. Atomic Reactor · Showing the uranium rods inserted horizontally and the control rods inserted vertically in the graphite block, which acts as a moderator to slow down the fission neutrons. A heavy concrete encasement protects workers from radiation. (From *Explaining the Atom*, by Selig Hecht. The Viking Press, Inc., 1947)

There are various types of reactors, depending upon what nuclear fuel and what moderator are used. The reactors operated for power may use natural uranium (p. 364), or plutonium, or highly enriched or slightly enriched uranium, or even U^{233}, a fissionable isotope derived from thorium. Except for the few neutrons required at the start, all the neutrons that maintain the chain reaction in the reactor are supplied by the fissioning nuclei (p. 361 and Fig. 21-4). But these fission neutrons have a high velocity, about 10,000 miles per second. (1) They must be slowed down a great deal, by passage through a "moderator," if they are to have a good chance of being captured by the nuclei of the atomic fuel, which will then undergo fission or transmutation. (2) On the other hand, to keep the chain reaction from building up to a rate that is too great, some of the neutrons may have to be removed; and this can be done with some substance that absorbs neutrons. By exercising control over (1) and (2) together, control of the over-all rate of the reaction in the reactor can be secured.

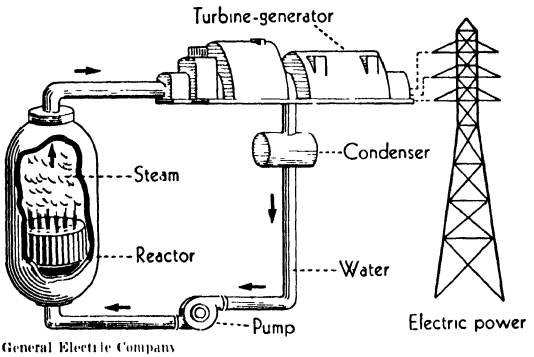
Graphite is an effective moderator; and some reactors have been constructed out of blocks of graphite drilled with slots (Fig. 47–4). Control of the rate of the reaction, in the case where uranium is the fuel, is secured by varying the extent to which (1) the uranium rods (p. 364), and (2) rods of *cadmium* or *boron steel* ("control rods" which absorb neutrons), are pushed into the graphite.

A similar graphite reactor at Oak Ridge is operated relatively "cold," for the sake of obtaining the fission products and of preparing various

radioactive isotopes by neutron bombardment of samples introduced into the reactor. This is the source of most of the radiotracers used in chemical and medical research.

In other reactors the moderator may be heavy water, D_2O, or beryllium. It is not necessary that the fuel be a pure metal. It may be an alloy, or a compound, like an oxide or a salt. If the isotope U^{238} of natural uranium is being converted to plutonium in the reactor, the nuclear reaction is said to be "breeding." Not only can one reap the benefit of the tremendous yield of energy, but the material product of the reaction, the plutonium, is itself a nuclear fuel. It is produced in an amount about equal to the U^{238} that is consumed, and if all of the U^{238} were to be consumed, 140 times as much plutonium as the U^{235} originally present would be produced.

It is important to realize that such reactors do not in themselves produce mechanical or electrical energy; they produce heat. As shown in Fig. 47-5, a reactor is like the furnace or fire pot of a boiler in which steam is being generated; though often the heat is carried away from the reactor by a molten metal or molten salt to a heat exchanger or boiler where the steam is made.



General Electric Company

Fig. 47-5. Atomic Power Plant · Showing production of heat in reactor, and steam, as in a boiler

The Carnot efficiency of the operation (p. 794) is involved in an interesting way. The higher the temperature T_2 of the reactor, and consequently of the steam, for a given condenser temperature T_1, the greater the efficiency of conversion of heat to work in the engine or turbine. But the higher temperature makes it more difficult to moderate, or slow down, the high velocity of the neutrons and secure efficient capture of them by atoms of U^{238}. One of the desirable effects is helped by higher temperature, the other one is hindered.

Progress in Perfecting Reactors · Among the many difficult problems connected with the design and operation of reactors, the most difficult is the problem of shielding out the extremely dangerous and penetrating gamma radiations. A shield of concrete should be at least 6 feet thick. In recent years several reactor installations have been built to supply power to fairly large communities in various countries. Reactors have

been used successfully in submarines, and progress is reported for installations in aircraft. In the case of an automobile, however, it has been estimated that the shielding that would be required to give adequate protection to the occupants, as well as to the pedestrians who might come near the car, might weigh as much as 25 tons.

Advantage of Nuclear Fuel · The great advantage of a nuclear fuel is its relatively small bulk. One pound of uranium is equivalent in available energy to 10 or 15 million pounds of oil or coal. If 5 or 6 billion tons of good coal would supply the entire world's annual energy requirement of 40 trillion horsepower-hours, a mere 400 tons of uranium metal would do the same; and such a quantity of nuclear fuel could be delivered in a few trucks or planes. It is this small fuel requirement which makes the use of reactors so important to submarines, since it practically eliminates the need for refueling. Distant and inaccessible places not naturally possessing satisfactory energy resources, could easily be supplied with nuclear fuel.

Available Reserves · It has been estimated that the available reserve of uranium runs to 25 million tons, and that its energy equivalent is at least 20 times that of the coal reserves. It is to be noted that the natural thorium atom, ${}_{90}Th^{232}$, will capture a neutron and then emit two beta particles to give ${}_{92}U^{233}$, which, like plutonium, is an artificial fissionable atom; and that thorium is a considerably more abundant element than uranium. Nevertheless, the better-grade deposits of such nuclear fuels are not renewable (except in the limited sense of the "breeder"), and we may be wise enough not to exploit these resources, as we have in the case of our fossil fuels, with reckless extravagance.

If it were possible for us to learn how to "tame" the hydrogen bomb, and thus arrange a controlled fusion of hydrogen atoms, or other light atoms, we could probably find in the process a virtually inexhaustible source of energy.

Solar Energy · The sun's radiation is the prime source of all our energy; it is virtually an inexhaustible source, and also a very abundant source. In the sunshine that falls on the earth during a year there is energy equal to a million trillion horsepower-hours. This is 25,000 times the 40 trillion horsepower-hours that is our present annual energy requirement; and in one day we receive 70 times as much as we use in a year. As we come to realize more fully that we are making heavy inroads upon our stores of coal, oil, and gas, and that our reserve of nuclear fuel is not unlimited, we shall be concerned more and more seriously with the possibilities of converting sunshine directly to our use.

Sunshine energy can be useful to us (1) simply as heat, or as it is con-

verted (2) to mechanical energy, (3) to electrical energy, or (4) to chemical energy, as in photosynthesis. Let us consider these several forms of energy.

1. **Heat.** We have already noted that we receive from sunlight, depending upon geographic location, an average of 1 to 2 calories per square centimeters per minute, or from 138 to 275 calories per square yard per second. Attempts have been made to collect the heat and use it to warm houses and even to store it.

Window glass is a good trap for heat energy, since it passes most of the sun's light and heat coming from the outside, but stops the longer waves that are reradiated back to it from the inside. This is why hothouses are made of glass, and why a car with its windows closed becomes so hot inside. Several layers of especially clear glass, backed by a sheet of black copper, make a good absorber for the sun's energy. Such an absorber is used in the house-heating arrangement shown in Fig. 47-6. Many homes are comfortably heated through the winter; and even in a climate like that of Boston, a house may receive the major part of its heat from the sun if the area of the collector is as large as about one-fifth that of the wall and roof area of the house.

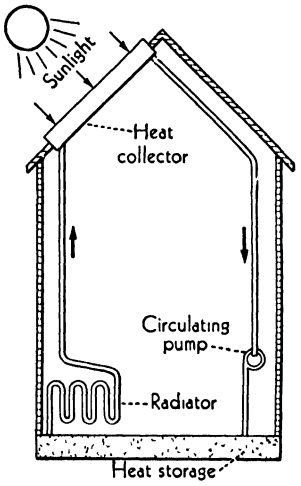


Fig. 47-6. Solar Energy · Showing how energy from the sun can be trapped and stored for heating. (By permission from *Energy Sources—The Wealth of the World*, by Ayres and Scarlott. Copyright, 1952. McGraw-Hill Book Company, Inc.)

Heat may be stored for several days in large, enclosed beds of pebbles, which absorb heat from hot air and give it out again to cool air; or heat may be stored by melting hydrated salts, like sodium sulfate, $Na_2SO_4 \cdot 10\ H_2O$, which melts and dehydrates simultaneously, and using the heat released when the melt freezes (and rehydrates) to warm cool air.

2. **Mechanical energy.** At the high Carnot efficiency (p. 794) of 95 per cent, and with a perfect engine, we could convert most of the heat, 138–275 calories, that falls upon a square yard in one second, into useful work. Two hundred and thirty-nine calories per second corresponds to 1000 watts, or $1\frac{1}{3}$ horsepower per square yard. On an acre, containing 4840 square yards, one might expect to get 6450 horsepower. Actually the power yield is far less.

Recent studies on the concentration of sunshine with focused mirrors suggest that under favorable conditions there might be a yield of 50 horsepower per acre, an efficiency of less than 1 per cent.

3. **Electrical energy.** Many attempts have been made to employ *thermocouples* in the conversion of sunshine into electrical energy, but with no noteworthy success. But now a *photovoltaic cell*, or *polar battery*, is under development in the Bell Telephone Laboratories. The cells are made of wafers of specially prepared silicon which are extremely sensitive to light, and can be linked together electrically to deliver a power of 110 watts from sunshine having a maximum power of 1000 watts per square yard. Thus the efficiency is about 11 per cent, and it may become as large as 22 per cent. Such cells, operated under the same conditions as focused mirrors, might yield about 700 horsepower per acre.

4. **Chemical energy.** Photosynthesis is a synthesis of chemical compounds with the aid of the energy of sunlight, in the presence of the chlorophyll in the green leaves of plants (p. 108). The radiant energy is absorbed and stored as chemical energy. A whole set of chemical reactions occurs; but the general nature of the process may be represented by the equation

$$H_2O + CO_2 + 112{,}000 \text{ cal} \underset{\text{(combustion)}}{\overset{\text{(sunlight)}}{\rightleftharpoons}} (\text{carbohydrates}) + O_2$$

Water vapor and carbon dioxide of the atmosphere are the starting materials. They diffuse into the leaf, and there the reaction occurs. The reaction to the right is not spontaneous. It is driven, uphill, by the energy absorbed from sunlight; and 112,000 calories are required to bring about the reaction between a mole of H_2O and a mole of CO_2. The water vapor and the carbon dioxide in themselves absorb little, if any, sunlight. The chlorophyll traps the energy and passes it on to the reactants.

On the product side of the equation, the carbohydrates may be sugars, starches, cellulose (p. 544). Oxygen is formed and liberated into the atmosphere. In fact, the oxygen present today in our atmosphere is probably the product of the photosynthesis reaction (p. 108).

The reaction is reversible. The carbohydrate will burn in the oxygen, producing water and carbon dioxide, and giving off 112,000 calories of heat, the same quantity of energy that was absorbed originally from the sun's radiation by the forward reaction. In this sense 112,000 calories of the sun's energy has been stored in the pair of substances, the carbohydrate, which may be considered to be a fuel—in fact, a very good fuel—and the oxygen.

One of the most puzzling things about the process is the fact that as much as 112,000 calories of energy is taken from light. Most of the light absorbed is red, having a wave length of about 6600 Å; and usually absorption of light of this wave length by a mole of reactant does not yield more than 40,000 calories for chemical reaction.

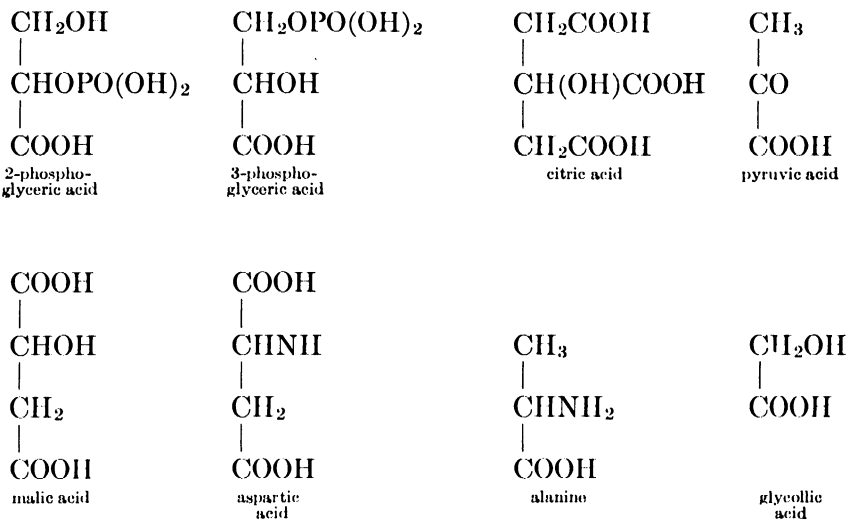
The total quantity of energy stored by plants growing on land surfaces amounts to about 5×10^{14} horsepower-hours in a year; and this is 12 times the world's present annual requirement. The efficiency of the conversion to stored chemical energy is low, averaging from 0.1 to 0.3 per cent, even in our agricultural practice. The production of plant materials in the ocean is several times greater than on land.

Constructing the Theory of Photosynthesis · Many significant facts regarding photosynthesis have been found out by experiment; and some progress is being made toward assembling the parts of what we hope will eventually prove to be a satisfying theory of the process. For instance, it has recently been demonstrated that photosynthesis can take place outside the living cell of a plant with the use of the isolated chloroplasts, which are the minute, flattened granules in which the chlorophyll is located (p. 109); and we have learned that the oxygen that is liberated in the process comes from the water, and not from the carbon dioxide, as was formerly supposed. We shall describe very briefly a part of the work of Calvin and his associates at the University of California since, incidentally, it affords an apt illustration of the scientific method.

A theory, of which Van Niel was the principal author, had proposed that the process is definitely separable into two stages, (1) a reaction that goes only in the light (the separation of active hydrogen from the oxygen of water), followed by (2) a reaction that may occur in the dark (the reaction of the active hydrogen with carbon dioxide to form various compounds). Now, one of the steps in the application of the scientific method (p. 6) is to "test the theory"; and Calvin did this in the following way: He suspended a great many of the algae chlorella—tiny, one-celled plants containing chlorophyll—in water which was free of carbon dioxide, and illuminated them to bring about reaction (1). Then a measured volume of the illuminated suspension was introduced quickly into a darkened vessel containing a water solution of carbon dioxide. Reaction (2), the reduction in the dark of the carbon dioxide by the active hydrogen, did indeed start. It was allowed to continue for a measured length of time and then stopped by an addition of hot alcohol. The compounds formed were extracted, and identified by sensitive modern analytical methods, including the use of radiotracers, especially of carbon-14 (p. 365).

Thus is the chemist able not only to check the theory but, during the course of the experiments designed to make the test, to discover new and significant facts. Of the compounds that are formed in reaction (2) during the first minute we may mention the following (some of their formulas are given below): ribulose phosphate (a phosphoric acid ester of a pentose), 2-phosphoglyceric acid and 3-phosphoglyceric acid, citric acid,

pyruvic acid, malic acid, aspartic acid, glycine, alanine, glucose, sucrose, and others, including compounds of phosphorus and sulfur. During the first 5 seconds the first seven of the compounds just listed are formed. Ribulose phosphate and citric acid are produced almost instantly.



There are eleven different stages catalyzed by enzymes, and eleven intermediate compounds, between the original simple ingredients and the high-energy compounds finally formed, as well as at least two cycles in which the compounds come successively into being as though on an assembly line.

Conclusion · We recognize that the photosynthesis reactions are complicated, and that we have made a mere beginning in understanding them. But we realize that it is of great importance that studies of these reactions continue as intensively as possible. There is a good chance that we can improve the efficiency of conversion of light to the chemical energy of fuel and food at least in our agricultural practices; and further, basing our thinking on what we have already learned, and on what we continue to learn from nature about the mechanisms of the process, there is always the chance that we can beat nature at her own game and think up a much simpler, more direct, more effective method of utilizing the sun's energy.

Many hundreds of able scientists—chemists, physicists, biologists—have joined in the search for understanding of the photosynthesis reactions. These investigations are among the most fascinating adventures of modern times; and the great economic significance of a successful outcome adds zest to the enterprise.

APPENDIX

Chemical Library

The student interested in chemistry will profit not only from systematic reading but also from browsing in a good chemical library. The following list of journals and books is but a sampling of the wealth of literature available to him. The authors believe that judicious use of this resource material can enrich materially a student's experience in the first course in chemistry.

JOURNALS

For weekly readings of current science news:

Science News Letter, published by Science Service, Washington, D. C. High lights of the week in all the sciences.

Chemical and Engineering News, published by the American Chemical Society, Easton, Pennsylvania. News of the week in chemistry as well as articles on general topics in chemistry and chemical industry.

Science, published by Science Press, Lancaster, Pennsylvania. The weekly news of the American Association for the Advancement of Science, together with articles of an advanced nature on topics in all fields of science.

For monthly readings of current science news:

Journal of Chemical Education, published by the Division of Chemical Education of the A. C. S., Easton, Pennsylvania. Timely articles reviewing various aspects of chemistry, written for the teacher of chemistry and the beginning student.

Scientific American, published by Scientific American, Inc., New York. Contains excellent articles on chemistry and other branches of science written by recognized authorities.

There are also many journals that contain articles of an advanced nature in all fields of chemistry. Some of these are the *Journal of the American Chemical Society*, *Journal of Organic Chemistry*, *Journal of Physical Chemistry*, *Industrial and Engineering Chemistry*, *Journal of Agricultural Chemistry*, and *Analytical Chemistry*, all published by the American Chemical Society, Easton, Pennsylvania.

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ELECTRONIC CONFIGURATIONS OF THE ATOMS

	AT NO	ELEMENT	NUMBER OF ELECTRONS IN EACH ELECTRON (QUANTUM) GROUP												
			1 *s*	2 *s*	2 *p*	3 *s*	3 *p*	3 *d*	4 *s*	4 *p*	4 *d*	4 *f*	5 *s*	5 *p*	5 *d*
	1	H	1												
	2	He	2												
	3	Li	2	1											
	4	Be	2	2											
	5	B	2	2	1										
	6	C	2	2	2										
	7	N	2	2	3										
	8	O	2	2	4										
	9	F	2	2	5										
	10	Ne	2	2	6										
	11	Na	2	2	6	1									
	12	Mg	2	2	6	2									
	13	Al	2	2	6	2	1								
	14	Si	2	2	6	2	2								
	15	P	2	2	6	2	3								
	16	S	2	2	6	2	4								
	17	Cl	2	2	6	2	5								
	18	A	2	2	6	2	6								
	19	K	2	2	6	2	6		1						
	20	Ca	2	2	6	2	6		2						
Transition elements	21	Sc	2	2	6	2	6	1	2						
	22	Ti	2	2	6	2	6	2	2						
	23	V	2	2	6	2	6	3	2						
	24	Cr	2	2	6	2	6	5	1						
	25	Mn	2	2	6	2	6	5	2						
	26	Fe	2	2	6	2	6	6	2						
	27	Co	2	2	6	2	6	7	2						
	28	Ni	2	2	6	2	6	8	2						
	29	Cu	2	2	6	2	6	10	1						
	30	Zn	2	2	6	2	6	10	2						
	31	Ga	2	2	6	2	6	10	2	1					
	32	Ge	2	6	6	2	6	10	2	2					
	33	As	2	2	6	2	6	10	2	3					
	34	Se	2	2	6	2	6	10	2	4					
	35	Br	2	2	6	2	6	10	2	5					
	36	Kr	2	2	6	2	6	10	2	6					
	37	Rb	2	2	6	2	6	10	2	6			1		
	38	Sr	2	2	6	2	6	10	2	6			2		
Transition elements	39	Y	2	2	6	2	6	10	2	6	1		2		
	40	Zr	2	2	6	2	6	10	2	6	2		2		
	41	Nb	2	2	6	2	6	10	2	6	4		1		
	42	Mo	2	2	6	2	6	10	2	6	5		1		
	43	Tc	2	2	6	2	6	10	2	6	6		1		
	44	Ru	2	2	6	2	6	10	2	6	7		1		
	45	Rh	2	2	6	2	6	10	2	6	8		1		
	46	Pd	2	2	6	2	6	10	2	6	10				
	47	Ag	2	2	6	2	6	10	2	6	10		1		
	48	Cd	2	2	6	2	6	10	2	6	10		2		
	49	In	2	2	6	2	6	10	2	6	10		2	1	
	50	Sn	2	2	6	2	6	10	2	6	10		2	2	

		AT NO	ELEMENT	NUMBER OF ELECTRONS IN EACH ELECTRON (QUANTUM) GROUP																	
				1 *s*	2 *s*	2 *p*	3 *s*	3 *p*	3 *d*	4 *s*	4 *p*	4 *d*	4 *f*	5 *s*	5 *p*	5 *d*	5 *f*	6 *s*	6 *p*	6 *d*	7 *s*	7 *p*
		51	Sb	2	2	6	2	6	10	2	6	10		2	3							
		52	Te	2	2	6	2	6	10	2	6	10		2	4							
		53	I	2	2	6	2	6	10	2	6	10		2	5							
		54	Xe	2	2	6	2	6	10	2	6	10		2	6							
		55	Cs	2	2	6	2	6	10	2	6	10		2	6			1				
		56	Ba	2	2	6	2	6	10	2	6	10		2	6			2				
Transition elements	Rare earths	57	La	2	2	6	2	6	10	2	6	10		2	6	1		2				
		58	Ce	2	2	6	2	6	10	2	6	10	2	2	6			2				
		59	Pr	2	2	6	2	6	10	2	6	10	3	2	6			2				
		60	Nd	2	2	6	2	6	10	2	6	10	4	2	6			2				
		61	Pm	2	2	6	2	6	10	2	6	10	5	2	6			2				
		62	Sm	2	2	6	2	6	10	2	6	10	6	2	6			2				
		63	Eu	2	2	6	2	6	10	2	6	10	7	2	6			2				
		64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2				
		65	Tb	2	2	6	2	6	10	2	6	10	9	2	6			2				
		66	Dy	2	2	6	2	6	10	2	6	10	10	2	6			2				
		67	Ho	2	2	6	2	6	10	2	6	10	11	2	6			2				
		68	Er	2	2	6	2	6	10	2	6	10	12	2	6			2				
		69	Tm	2	2	6	2	6	10	2	6	10	13	2	6			2				
		70	Yb	2	2	6	2	6	10	2	6	10	14	2	6			2				
		71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2				
		72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2				
		73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2				
		74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2				
		75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2				
		76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2				
		77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	9						
		78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1				
		79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1				
		80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2				
		81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1			
		82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2			
		83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3			
		84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4			
		85	At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5			
		86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			
		87	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1	
		88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2	
		89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2	
		90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2	
		91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2	
		92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2	
		93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2	
		94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2	
		95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2	
		96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2	
		97	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2	
		98	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	9	2	6	1	2	
		99	E	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	1	2	
		100	Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	1	2	
Transition elements (actinides)		101	Mv	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	1	2	

Reference Tables

DENSITIES AND MELTING POINTS OF SOME OF THE MORE COMMON ELEMENTS

NAME	DENSITY	MELTING POINT	NAME	DENSITY	MELTING POINT
Aluminum	2.702	660°	Mercury (liquid)	13.546	− 38.87°
Antimony	6.684	630.5°	Molybdenum	10.2	2625°
Arsenic (metallic)	5.7	814°36 atm	Nickel	8.90	1452°
Barium	3.5	850°	Palladium	12.0	1555°
Bismuth	9.80	271°	Phosphorus (red)	2.20	590°43 atm
Boron	2.5	2300°	Phosphorus (yellow)	1.82	44.1°
Bromine (liquid)	3.119	− 7.2°	Platinum	21.45	1755°
Cadmium	8.6	320.9°	Potassium	0.86	62.3°
Calcium	1.55	810°	Radium	5(?)	960°(?)
Carbon (diamond)	3.51	——	Selenium (gray)	4.80	220°
Carbon (graphite)	2.26	3500°	Silicon	2.4	1420°
Chromium	7.1	1615°	Silver	10.5	960.5°
Cobalt	8.9	1480°	Sodium	0.97	97.5°
Copper	8.92	1083°	Strontium	2.6	800°
Gallium	5.91	29.75°	Sulfur (monoclinic)	1.96	119.0°
Gold	19.3	1063°	Sulfur (rhombic)	2.07	112.8°
Iodine	4.93	113.5°	Tantalum	16.6	2850°
Iridium	22.4	2350°	Tellurium (metallic)	6.24	452°
Iron	7.86	1535°	Tin (white, tetragonal)	7.31	231.85°
Lead	11.34	327.5°	Titanium	4.5	1800°
Lithium	0.53	186°	Tungsten	19.3	3370°
Magnesium	1.74	651°	Vanadium	5.96	1710°
Manganese	7.2	1260°	Zinc	7.14	419.43°

WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS; BOILING POINTS UNDER PRESSURE OF 760 MILLIMETERS

NAME	WEIGHT OF 1 LITER	BOILING POINT	NAME	WEIGHT OF 1 LITER	BOILING POINT
Acetylene	1.1621	− 83.6°	Hydrogen chloride	1.6398	− 85.0°
Air	1.2930		Hydrogen sulfide	1.5392	− 59.6°
Ammonia	0.7708	− 33.3°	Methane	0.7168	− 161.4°
Argon	1.7824	− 185.7°	Nitric oxide	1.3402	− 151.0°
Carbon dioxide	1.9768	sublimes	Nitrogen	1.2506	− 195.8°
Carbon monoxide	1.2504	− 192.0°	Nitrous oxide	1.9777	− 89.5°
Chlorine	3.214	− 34.6°	Oxygen	1.4290	− 183.0°
Helium	0.1785	− 268.9°	Propane	2.0200	− 45.0°
Hydrogen	0.08987	− 252.7°	Sulfur dioxide	2.9266	− 10.0°

ELECTROCHEMICAL SERIES

1. Lithium
2. Potassium
3. Calcium
4. Sodium
5. Magnesium
6. Aluminum
7. Manganese
8. Zinc
9. Chromium
10. Iron
11. Cadmium
12. Cobalt
13. Nickel
14. Tin
15. Lead
16. Hydrogen
17. Bismuth
18. Copper
19. Mercury
20. Silver
21. Platinum
22. Gold

SOLUBILITIES OF SOME OF THE COMPOUNDS OF THE MORE COMMON METALS

	Acetate	Bromide	Carbonate	Chlorate	Chloride	Chromate	Hydroxide	Iodide	Nitrate	Oxide	Phosphate	Silicate (ortho)	Sulfate	Sulfide
Aluminum	W	W		W	W		A	W	W	A–I	A	A–I	W	H–A
Ammonium	W	W	W	W	W	W	W	W	W		W		W	W
Barium	W	W	A	W	W	A	W	W	W	W	A	A	I	W
Calcium	W	W	A	W	W	W–A	W–A	W	W	W–A	A	A	W–I	W–A
Cobalt	W	W	A	W	W	A	A	W	W	A	A	A	W	A
Copper	W	W	A	W	W	W	A	A	W	A	A	A	W	A–N
Ferric	W	W		W	W	W	A	W	W	A	A	A	W	A
Ferrous	W	W	A	W	W		A	W	W	A	A	A	W	A
Lead	W	W–A	A	W	W–I	A–I	A	W–A	W	A	A	A	A–I	A
Magnesium	W	W	A	W	W	W	A	W	W	A	A	A	W	H–A
Manganese	W	W	A	W	W	A	A	W	W	A	A	A	W	A
Mercuric	W	W	A	W	W	W–A	A	A	W	A	A		H–A	A–R
Mercurous	W–A	A	H–A	W	A–I	A		A–N	W	A	A–N		W–A	A–I
Nickel	W	W	A	W	W	A	A	W	W	A	A	A	W	A
Potassium	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Silver	W–A	I	H–A	W	I	A		I	W	A	A	A	W–A	A
Sodium	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Stannous	W	W	A	W	W	A	A	W		A	A		W	A
Zinc	W	W	A	W	W	A	A	W	W	A	A	A	W	A

W, soluble in water.
A, insoluble in water, soluble in HCl or HNO_3, or both.
A–N, insoluble in water, soluble in HNO_3, and either insoluble in HCl or less soluble than in HNO_3.
I, insoluble in water, HCl, and HNO_3.
H, hydrolyzed by water.
W–A, slightly soluble in water, soluble in acids.
A–I, insoluble in water, slightly soluble in acids.
W–I, slightly soluble in water and in acids.
A–R, soluble only in aqua regia.
H–A, hydrolyzed by water, soluble in acids.

THE NATURAL ISOTOPES OF THE ELEMENTS

The isotopes of each element are listed in the order of abundance (the most abundant being given first). Values in parentheses lack verification. A dash (- ——) signifies that the element has no natural isotopes. The table lists only natural isotopes. Approximately 322 natural isotopes and 498 artificial isotopes are known today

ATOMIC NUMBER	SYMBOL AND ATOMIC WEIGHT	NATURAL ISOTOPES (MASS NUMBERS)
1	H 1.0080	1, 2
2	He 4 003	4, 3
3	Li 6.940	7, 6
4	Be 9.02	9
5	B 10.82	11 10
6	C 12.010	12, 13
7	N 14.008	14, 15
8	O 16.000	16, 18, 17
9	F 19.00	19
10	Ne 20.183	20, 22, 21
11	Na 22 997	23
12	Mg 24.32	24, 25, 26
13	Al 26.97	27
14	Si 28.06	28, 29, 30
15	P 30.98	31
16	S 32.06	32, 34, 33, 36
17	Cl 35 457	35, 37
18	A 39 944	40, 36, 38
19	K 39.096	39, 41, 40
20	Ca 40 08	40, 44, 42, 48, 43, 46
21	Sc 45.10	45
22	Ti 47.90	48, 46, 47, 49, 50
23	V 50.95	51
24	Cr 52.01	52, 53, 50, 54
25	Mn 54.93	55
26	Fe 55.85	56, 54, 57, 58
27	Co 58.94	59
28	Ni 58.69	58, 60, 62, 61, 64
29	Cu 63.57	63, 65
30	Zn 65.38	64, 66, 68, 67, 70
31	Ga 69.72	69, 71
32	Ge 72.60	74, 72, 70, 73, 76
33	As 74 91	75
34	Se 78.96	80, 78, 76, 82, 77, 74
35	Br 79.916	79, 81
36	Kr 83 7	84, 86, 82, 83, 80, 78
37	Rb 85.48	85, 87
38	Sr 87.63	88, 86, 87, 84
39	Y 88.92	89
40	Zr 91.22	90, 94, 92, 91, 96
41	Nb 92.91	93
42	Mo 95.95	98, 96, 95, 92, 94, 97, 100
43	Tc	— —
44	Ru 101.7	102, 104, 101, 99, 100, 96, 98
45	Rh 102.91	103
46	Pd 106 7	106, 108, 105, 110, 104, 102
47	Ag 107.880	107, 109
48	Cd 112 41	114, 112, 111, 110, 113, 116, 106, 108
49	In 114.76	115, 113
50	Sn 118.70	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
51	Sb 121.76	121, 123
52	Te 127.61	130, 128, 126, 125 124, 122, 123, 120
53	I 126.92	127
54	Xe 131 3	132, 129, 131, 134, 136, 130, 128, 124, 126
55	Cs 132 91	133
56	Ba 137.36	138, 137, 136, 135, 134, 130, 132
57	La 138.92	139, 138
58	Ce 140 13	140, 142, 138, 136
59	Pr 140 92	141
60	Nd 144.27	142, 144, 146, 143, 145, 148, 150
61	Pm	——
62	Sm 150.43	152, 154, 147, 149, 148, 150, 144
63	Eu 152.0	153, 151
64	Gd 156 9	158, 160, 156, 157 155, 154, 152
65	Tb 159 2	159
66	Dy 162.46	164, 162, 163, 161, 158, 160
67	Ho 164.94	165
68	Er 167.2	166, 168, 167, 170, 164, 162
69	Tm 169 4	169
70	Yb 173.04	174, 172, 173, 171, 176 170 168
71	La 174.99	175, 176
72	Hf 178 6	180, 178, 177, 179, 176, 174
73	Ta 180.88	181
74	W 183.92	184, 186, 182, 180
75	Re 186.31	187, 185
76	Os 190 2	192, 190, 189, 188, 187, 186, 184
77	Ir 193 1	193, 191
78	Pt 195 23	195, 194, 196, 198, 192, 190
79	Au 197.2	197
80	Hg 200 61	202, 200, 199, 201, 198, 204, 196
81	Tl 204 39	205, 203, 206, 207, 208, 210
82	Pb 207.21	208, 206, 207, 204, 210, 211, 212, 214
83	Bi 209.00	209, 210, 211, 212, 214
84	Po	210, 211, 212, 214, 215, 216, 218
85	At	218, 215
86	Rn 222	222, 220. 219
87	Fr	223
88	Ra 226.05	223, 224, 226, 228
89	Ac	227, 228
90	Th 232.12	227, 228, 230, 231, 232, 234
91	Pa 231	231, 234
92	U 238.07	238, 235, 234
93	Np	——
94	Pu	239
95	Am	— —
96	Cm	——
97	Bk	——
98	Cf	——
99	E	——
100	Fm	——
101	Mv	——

VAPOR PRESSURE OF WATER EXPRESSED IN MILLIMETERS OF MERCURY

(International Critical Tables)

TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE
10°	9.209	21°	18.650	32°	35.663
11°	9.844	22°	19.827	33°	37.729
12°	10.518	23°	21.068	34°	39.898
13°	11.231	24°	22.377	35°	42.175
14°	11.987	25°	23.756	36°	44.563
15°	12.788	26°	25.209	37°	47.067
16°	13.634	27°	26.739	38°	49.692
17°	14.530	28°	28.349	39°	52.442
18°	15.477	29°	30.043	40°	55.324
19°	16.477	30°	31.824	50°	92.51
20°	17.535	31°	33.695	100°	760.00

RELATIONSHIP BETWEEN VARIOUS UNITS OF MEASUREMENT

1 lb (troy) = 373.24 g
1 oz (troy) = 31.10348 g
1 lb (avoirdupois) = 453.59 g
1 oz (avoirdupois) = 28.350 g
1 kg = 2.67923 lb (troy)
1 kg = 2.20462 lb (avoirdupois)
1 liter = 1.05668 United States liquid qt
1 gal (U.S.) = 3.78543 liters
1 gal (imperial) = 4.5460 liters

1 ml = 0.0610 cu in.
1 cu in. = 16.3872 ml
1 cu ft = 28,317 ml
1 cm = 0.3937 in.
1 m = 39.37 in.
1 km = 0.62137 miles
1 cal = 0.003968 Btu
1 Btu = 252 cal

1 mm (Hg) = 0.019337 lb/sq in.
1 lb/sq in. = 51.715 mm (Hg)
$C° = (F° - 32°) \times \frac{5}{9}$; $F° = (C° \times \frac{9}{5}) + 32°$
0° (on absolute scale, or Kelvin scale) = − 273° C
0° (on absolute Fahrenheit scale, or Rankine scale) = − 460° F
Standard conditions: 0° C (273° A), 760 mm = 32° F (492° Rankine), 14.7 lb/sq in

Some Fundamental Arithmetical Operations

Many of the important relationships and much of the satisfying logic of chemistry come to light only after quantitative treatment of observations. Any quantitative study involves an attempt to establish number relationships and calls for the use of arithmetic. In this section some suggestions are made, and some examples given, that may prove helpful to the student in connection with (1) calculation by the method of ratios and proportion, (2) the calculation of percentages, (3) the expression of very large and very small numbers as powers of 10, and (4) the use of units, particularly English units instead of cgs units.

1. ***Ratio and Proportion*** · Every student has at one time or another used the method of "proportion" to solve a problem. A proportion, in the sense in which it is used here, consists of two ratios which are equal to each other. For example, in the proportion $\frac{A}{B} = \frac{C}{D}$, A is related to B in the same way as C is related to D; and the proportion is read: "A is to B as C is to D." The thing about a

proportion that makes it helpful is the fact that if three of the four terms are known, the fourth can always be calculated. Take the proportion $\frac{1}{15} = \frac{x}{90}$. Solution for x gives $x = 6$; and of course 6 is related to 90 in the same way as 1 is related to 15.

Let us consider a further example: If it requires 15 minutes for a train traveling at a constant speed to go 10 miles, how long will it take the train to go 25 miles? To solve this problem we use two ratios and a proportion.

The ratios are $\frac{15 \text{ minutes to go}}{10 \text{ miles}}$ and $\frac{x \text{ minutes to go}}{25 \text{ miles}}$.

The proportion is $\frac{15 \text{ minutes}}{10 \text{ miles}} = \frac{x \text{ minutes}}{25 \text{ miles}}$.

$$x = \frac{15 \text{ minutes} \times 25 \cancel{\text{ miles}}}{10 \cancel{\text{ miles}}} = 37.5 \text{ minutes.}$$

Chemists use the method of ratios and proportion in solving many of their problems.

Example 1. How many centimeters are equivalent to 12 in. if there are 2.54 cm in 1 in.?

The ratios are $\frac{2.54 \text{ cm are equivalent to}}{1 \text{ in.}}$ and $\frac{x \text{ cm are equivalent to}}{12 \text{ in.}}$.

The proportion is $\frac{2.54 \text{ cm}}{1 \text{ in.}} = \frac{x \text{ cm.}}{12 \text{ in.}}$.

$$x = \frac{2.54 \text{ cm} \times 12 \cancel{\text{ in.}}}{1 \cancel{\text{ in.}}} = 30.48 \text{ cm.}$$

Example 2. Calculate the weight of iron that can be obtained from 1 ton of iron ore if 56 tons of iron can be obtained from 72 tons of iron ore.

The ratios are $\frac{72 \text{ tons of iron ore give}}{56 \text{ tons of iron}}$ and $\frac{1 \text{ ton of iron ore gives}}{x \text{ tons of iron}}$.

The proportion is $\frac{72 \text{ tons ore}}{56 \text{ tons iron}} = \frac{1 \text{ ton ore}}{x \text{ tons iron}}$.

$$x = \frac{56 \text{ tons iron} \times 1 \cancel{\text{ ton ore}}}{72 \cancel{\text{ tons ore}}} = 0.78 \text{ ton of iron.}$$

Each of the foregoing problems involves a direct proportion, in which one variable quantity increases as another variable quantity increases. Often we must deal with an inverse proportion, in which one variable quantity increases as another variable quantity (on which it depends) *decreases*. Boyle's law is an example. Let us start with an original volume of gas, V_1, at an original pressure, P_1, and (while keeping the temperature constant) let the pressure increase to P_2. What will the final volume, V_2, be? *If* the volume were directly proportional to the pressure, the proportion would be $\frac{V_1}{V_2} = \frac{P_1}{P_2}$. But the volume is *inversely* proportional to the pressure; hence the proportion is $\frac{V_1}{V_2} = \frac{P_2}{P_1}$.

Example 3. Calculate the volume that a gas will occupy at 760 mm pressure if it occupies 100 ml at 380 mm.

The ratios are $\frac{100 \text{ ml}}{x \text{ ml}}$ and $\frac{380 \text{ mm}}{760 \text{ mm}}$.

The inverse proportion is $\frac{100 \text{ ml}}{x \text{ ml}} = \frac{760 \text{ mm}}{380 \text{ mm}}$.

$$x = \frac{100 \text{ ml} \times 380 \cancel{\text{ mm}}}{760 \cancel{\text{ mm}}} = 50 \text{ ml.}$$

2. ***Percentage*** · The chemist frequently expresses experimental data in per cents. The term *per cent*, from the Latin phrase *per centum*, means "parts per hundred" (literally, "by the hundred"). Thus the statement that 11.18 per cent by weight of water is hydrogen means that there are 11.18 parts by weight of hydrogen in 100 parts by weight of water. This ratio holds, regardless of the units of weight used; there are 11.18 g of hydrogen in 100 g of water, and 11.18 lb of hydrogen in 100 lb of water.

Problems involving the calculation of percentage or calculations from given percentages may be *reduced to problems in proportion.* A problem asks, "If there are 48 g of oxygen in 122.5 g of potassium chlorate, what per cent by weight of potassium chlorate is oxygen?" This may be restated to read as follows: "If there are 48 parts by weight of oxygen in 122.5 parts by weight of potassium chlorate, how many parts by weight of oxygen are there in 100 parts by weight of potassium chlorate?" To solve this problem by the method of ratios and proportion, we may proceed as follows:

The ratios are $\frac{48 \text{ parts } O_2}{122.5 \text{ parts } KClO_3}$ and $\frac{x \text{ parts } O_2}{100 \text{ parts of } KClO_3}$.

The proportion is $\frac{48 \text{ parts } O_2}{122.5 \text{ parts } KClO_3} = \frac{x \text{ parts } O_2}{100 \text{ parts } KClO_3}$.

$$x = \frac{48 \text{ parts } O_2 \times 100 \text{ parts } \cancel{KClO_3}}{122.5 \text{ parts } \cancel{KClO_3}}.$$

$x = 39$ parts O_2 in 100 parts $KClO_3$;

$x = 39$ per cent O_2.

Similarly the problem "How much copper is there in 450 g of copper sulfate if 25.6 per cent of copper sulfate is copper?" really asks, "How much copper is there in 450 g of copper sulfate if 100 g of copper sulfate contains 25.6 g of copper?"

The ratios are $\frac{100 \text{ g } CuSO_4 \text{ contains}}{25.6 \text{ g Cu}}$ and $\frac{450 \text{ g } CuSO_4 \text{ contains}}{x \text{ g Cu}}$.

The proportion is $\frac{100 \text{ g } CuSO_4}{25.6 \text{ g Cu}} = \frac{450 \text{ g } CuSO_4}{x \text{ g Cu}}$.

$$x = \frac{450 \text{ g } \cancel{CuSO_4} \times 25.6 \text{ g Cu}}{100 \text{ g } \cancel{CuSO_4}} = 115 \text{ g Cu.}$$

3. ***Exponential Arithmetic*** · *a.* **Large numbers.** Frequently chemists must use large numbers in their calculations. For instance, the number of molecules in a milliliter of air is about 27,000,000,000,000,000,000. We may avoid the labor of writing so many ciphers and express such numbers much more conveniently and compactly in terms of exponents of 10. Thus, the number just given, 27 quintillion, may be written as 27×10^{18}, where the *exponent* of 10 in-

dicates the number of ciphers to be added to the 27. Or it may preferably be written as 2.7×10^{19}. To show more fully how this system is employed in writing numbers, the following table is given:

$1 = 10^0$	$5 = 5 \times 10^0$
$10 = 10^1$	$50 = 5 \times 10^1$
$100 = 10^2$	$500 = 5 \times 10^2$
$100{,}000 = 10^5$	$537{,}000 = 5.37 \times 10^5$
$100{,}000{,}000 = 10^8$	$128{,}000{,}000 = 1.28 \times 10^8$
$1{,}000{,}000{,}000 = 10^9$	$1{,}280{,}000{,}000 = 1.28 \times 10^9$

b. **Small numbers.** Similarly the very small numbers which are often used in chemical calculations may be expressed in terms of the *negative* exponents of 10. A table will help to make the method clear:

$$0.1 = \frac{1}{10} = \frac{1}{10^1} = 10^{-1}$$

$$0.01 = \frac{1}{100} = \frac{1}{10^2} = 10^{-2}$$

$$0.0000001 = \frac{1}{10{,}000{,}000} = \frac{1}{10^7} = 10^{-7}$$

$$0.5 = 5 \times 10^{-1}$$

$$0.053 = 5.3 \times 10^{-2}$$

$$0.000013 = 1.3 \times 10^{-5}$$

$$0.0000008 = 8 \times 10^{-7}$$

As a further example, a piece of gold, just too small to be visible in the most powerful microscope, weighs about 0.000,000,000,000,019 g, or, expressed in the exponential system, 19×10^{-15} g, or 1.9×10^{-14} g.

c. **Calculations.** If numbers involving powers of 10 are to be added or subtracted, they must be expressed as the same powers of 10. Thus, in adding 4×10^{-2} and 5×10^{-3}, the latter number may be written as 0.5×10^{-2}; and this, added to 4×10^{-2}, gives 4.5×10^{-2}.

Exponential arithmetic is especially helpful and convenient in performing the multiplication and division of large and small numbers. For example, suppose we wish to multiply 32,100,000,000,000 by 3,000,000. We may write the two numbers as 3.21×10^{13} and 3×10^6. The 3.21 and 3 are multiplied together, and the *exponents* are added. The product is 9.63×10^{19}. If we multiply 3.21×10^{13} by 3×10^{-6}, the result is 9.63×10^7.

$$\begin{array}{r} 3.21 \times 10^{13} \\ 3 \times 10^{6} \\ \hline 9.63 \times 10^{19} \end{array} \qquad \begin{array}{r} 3.21 \times 10^{13} \\ 3 \times 10^{-6} \\ \hline 9.63 \times 10^{7} \end{array}$$

If we wish to divide 3.21×10^{13} by 3×10^6, the number 3.21 is divided by 3, and the exponent 6 is subtracted from the exponent 13. The quotient is 1.07×10^7. To divide 3.21×10^{13} by 3×10^{-6}, the number 3.21 is again divided by 3 and the exponent -6 is subtracted from the exponent 13. The result is 1.07×10^{19}.

$$\frac{3.21 \times 10^{13}}{3 \times 10^6} = 1.07 \times 10^7; \qquad \frac{3.21 \times 10^{13}}{3 \times 10^{-6}} = 1.07 \times 10^{19}.$$

With a little practice the student can easily acquire considerable skill with exponential arithmetic and save himself a great deal of time and labor.

4. ***Use of Units in Chemical Calculations*** · While the cgs system of units is used in most scientific work and generally in this book, English units are sometimes used, especially in engineering.

The choice of units is a matter of convenience or of custom. If English units are used, the numerical values for measured quantities and for proportionality constants will, of course, be different from the values that are obtained when cgs units are used.

Example 1. A certain quantity of gas occupies 32 cu ft under a pressure of 25 lb/sq in.; what will the volume be at 40 lb/sq in.? This is evidently a problem involving Boyle's law, as in Example 3 on page 822, and involves an inverse proportion.

The ratios are $\frac{32 \text{ cu ft}}{x \text{ cu ft}}$ and $\frac{25 \text{ lb/sq in.}}{40 \text{ lb/sq in.}}$

The inverse proportion is $\frac{32 \text{ cu ft}}{x \text{ cu ft}} = \frac{40 \text{ lb/sq in.}}{25 \text{ lb/sq in.}}$

$$x = \frac{25 \cancel{\text{lb/sq in.}} \times 32 \text{ cu ft}}{40 \cancel{\text{lb/sq in.}}} = 20 \text{ cu ft.}$$

An example of the use of English units has been given on page 161, where a problem is solved using pound-molecular weights instead of the more usual gram-molecular weights. We may illustrate further the use of units in some calculations based on the *general gas equation*. Let us first derive this equation.

We derived, on page 63, an equation that embodies the laws of Boyle, Charles, and Gay-Lussac: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$. The equation means that $\frac{PV}{T}$ is constant for a given quantity of gas: $\frac{PV}{T} = k$, or $PV = kT$. If the quantity of gas is chosen to be 1 g-mol. wt, or 1 mole (occupying 1 g-mol. volume, which is the same for all gases), the constant is the same for all gases and is conventionally written as R. The equation $PV = RT$ then holds for 1 mole of any gas. If more than 1 mole, or a fraction of a mole, is involved, the equation becomes $PV = \frac{w}{M}RT$, where w is the weight of the gas, and M is the molecular weight of the gas. This equation is called the *general gas equation.*

The numerical value of R can be determined from the volume, V, occupied by a given weight, w, of a gas of known molecular weight, M, at a measured pressure, P, and temperature, T. For example, we find for oxygen ($M = 32$)

$$V = 22{,}400 \text{ ml when } w = 32 \text{ g}, P = 760 \text{ mm}, T = 273° \text{ A.}$$

We then solve the general gas equation for R:

$$R = \frac{760 \times 32 \times 22{,}400}{32 \times 273}$$

$= 62{,}400$ mm-ml per degree absolute per gram-molecular weight.

We should employ this value of R in all calculations in which we use cgs units.

Example 2. Calculate the molecular weight of the gas of which 0.0567 g occupies 100 ml at 100° and 752 mm pressure (Example 2, p. 139).

$V = 100$ ml; $R = 62{,}400$; $w = 0.0567$ g;
$P = 752$ mm; $T = 383°$ A; $M = ?$ g.

$$M = \frac{wRT}{PV} = \frac{0.0567 \times 62{,}400 \times 383}{752 \times 100} = 18 \text{ g};$$

therefore the molecular weight is 18.

Example 3. Calculate the volume occupied by 8 g of sulfur dioxide at 27° and 722 mm.

$V = ?$; $R = 62{,}400$; $w = 8$ g;
$P = 722$ mm; $T = 300°$ A; $M = 64$ g (SO_2).

$$V = \frac{wRT}{MP} = \frac{8 \times 62{,}400 \times 300}{64 \times 722} = 3240 \text{ ml}.$$

If English units are used, the value of R is different. We find from experiment that for oxygen

$V = 359$ cu ft when $w = 32$ lb, $P = 14.7$ lb/ sq in., $T = 492°$ Rankine (p. 68).

$$R = \frac{14.7 \times 32 \times 359}{32 \times 492}$$

$= 10.71$ lb/sq in.-cu ft per degree Rankine per pound-molecular weight; and this value of R is that to be used with the English units.

Example 4. Calculate the molecular weight of the gas of which 2 lb occupies 50.4 cu ft at 140° F and 15 lb/sq in.

$V = 50.4$ cu ft; $R = 10.71$; $w = 2$ lb;
$P = 15$ lb/sq in.; $T = (460 + 140)°$ Rankine; $M = ?$ lb.

$$M = \frac{wRT}{PV} = \frac{2 \times 10.71 \times 600}{15 \times 50.4} = 17 \text{ lb};$$

therefore the molecular weight is 17.

Example 5. Calculate the volume occupied by 11 lb of carbon dioxide at 40° and 20 lb/sq in.

$V = ?$; $R = 10.71$; $w = 11$ lb;
$P = 20$ lb/sq in.; $T = (460 + 40)°$ Rankine; $M = 44$ lb (CO_2).

$$V = \frac{wRT}{MP} = \frac{11 \times 10.71 \times 500}{44 \times 20} = 66.9 \text{ cu ft}.$$

Note that the volume occupied by a pound-molecular weight under standard conditions is 359 cu ft; this is the quantity which corresponds to 22.4 liters in cgs units (the volume occupied by a gram-molecular weight under standard conditions). The number of molecules in a pound-molecular weight is 2.73×10^{26}, corresponding to the Avogadro number, 6.02×10^{23}, the number of molecules in a gram-molecular weight.

The two values of R given above, 62,400 mm-ml/° A/g-mol. wt and 10.71 lb/sq in.-cu ft/° Rankine/lb-mol. wt, should be memorized by the student.

Example 6. Calculate the volume of hydrogen, measured at 1200° F and 15 lb/sq in., which will be required to reduce 20 lb of copper oxide to copper, according to the equation

$$\underset{64}{CuO} + \underset{2}{H_2} \longrightarrow \underset{16}{Cu} + H_2O$$

From the equation, 2 lb of hydrogen is required for 80 lb of copper oxide; and x lb of hydrogen will be needed for 20 lb of copper oxide.

$$\frac{2}{x} = \frac{80}{20};$$

$$x = \frac{2 \times 20}{80} \text{ lb of hydrogen.}$$

This weight of hydrogen will occupy a volume V.

$V = ?$; $R = 10.71$; $w = x = \frac{2 \times 20}{80}$ lb;

$P = 15$ lb/sq in.; $T = 1660°$ Rankine; $M = 2$ lb (H_2).

$$V = \frac{wRT}{MP} = \frac{\frac{2 \times 20}{80} \times 10.71 \times 1660}{2 \times 15} = \frac{2 \times 20 \times 10.71 \times 1660}{80 \times 2 \times 15} = 296 \text{ cu ft.}$$

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Table of the Chemical Elements, Including Their Symbols, Their Atomic Numbers, and Their Atomic Weights

Name	Symbol	Atomic Number	Atomic Weight	Name	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	227.0*	Mercury	Hg	80	200.61
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Americium	Am	95	243.*	Neodymium	Nd	60	144.27
Antimony	Sb	51	121.76	Neon	Ne	10	20.183
Argon	A	18	39.944	Neptunium	Np	93	237.*
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Astatine	At	85	210.*	Niobium	Nb	41	92.91
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Berkelium	Bk	97	245.*	Osmium	Os	76	190.2
Beryllium	Be	4	9.013	Oxygen	O	8	16.000
Bismuth	Bi	83	209.00	Palladium	Pd	46	106.7
Boron	B	5	10.82	Phosphorus	P	15	30.98
Bromine	Br	35	79.916	Platinum	Pt	78	195.23
Cadmium	Cd	48	112.41	Plutonium	Pu	94	239.*
Calcium	Ca	20	40.08	Polonium	Po	84	210.
Californium	Cf	98	246.*	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Promethium	Pm	61	147.*
Cesium	Cs	55	132.91	Protactinium	Pa	91	231.
Chlorine	Cl	17	35.457	Radium	Ra	88	226.05
Chromium	Cr	24	52.01	Radon	Rn	86	222.
Cobalt	Co	27	58.94	Rhenium	Re	75	186.31
Copper	Cu	29	63.54	Rhodium	Rh	45	102.91
Curium	Cm	96	243.*	Rubidium	Rb	37	85.48
Dysprosium	Dy	66	162.46	Ruthenium	Ru	44	101.7
Einsteinium	E	99	255.	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fermium	Fm	100	255.	Silicon	Si	14	28.06
Fluorine	F	9	19.00	Silver	Ag	47	107.880
Francium	Fr	87	223.*	Sodium	Na	11	22.997
Gadolinium	Gd	64	156.9	Strontium	Sr	38	87.63
Gallium	Ga	31	69.72	Sulfur	S	16	32.066
Germanium	Ge	32	72.60	Tantalum	Ta	73	180.88
Gold	Au	79	197.2	Technetium	Tc	43	99.*
Hafnium	Hf	72	178.6	Tellurium	Te	52	127.61
Helium	He	2	4.003	Terbium	Tb	65	159.2
Holmium	Ho	67	164.94	Thallium	Tl	81	204.39
Hydrogen	H	1	1.0080	Thorium	Th	90	232.12
Indium	In	49	114.76	Thulium	Tm	69	169.4
Iodine	I	53	126.92	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.90
Iron	Fe	26	55.85	Tungsten	W	74	183.92
Krypton	Kr	36	83.7	Uranium	U	92	238.07
Lanthanum	La	57	138.92	Vanadium	V	23	50.95
Lead	Pb	82	207.21	Xenon	Xe	54	131.3
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.99	Yttrium	Y	39	88.92
Magnesium	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mendelevium	Mv	101	256.				

*The atomic weights marked with asterisks are uncertain, and in several cases depend on the method of manufacture. In these cases the mass numbers of the most common or most abundant isotopes are given.

All the other atomic weights are taken from the official table published in the *Journal of the American Chemical Society* in April, 1950.